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## ON SOME DOUBLE AND TRIPLE THIOCYANATES.

### I. INTRODUCTION.

BY H. L. WELLS.

Several investigations, dealing chiefly with the double salts of caesium thiocyanate with a number of other thiocyanates, were undertaken in this laboratory during the past winter. This work was taken up because comparatively few double thiocyanates were known, and since several of those which had been described appeared to have compositions at variance with the known double chlorides, bromides, and iodides. After a number of double salts had been prepared, some of which proved to be unusually interesting, a very remarkable triple thiocyanate was accidentally made.

This triple salt was of so much interest that our original plans were considerably modified and much attention was then given to the preparation of other triple salts. Work was continued, however, on such double salts as might possibly throw light upon the nature of the curious triple salts.

The work with the triple thiocyanates, as far as it has gone,

shows that these compounds exist in great variety, and that a practically new, and probably important, field of inorganic chemistry has been opened up by their discovery.

The object of this introduction is to present the results thus far obtained in a concise form and to discuss them to some extent. Since the experimental details are given in subsequent articles, it may be mentioned here that no product has been accepted as a chemical compound that was not well and homogeneously crystallized, and that every formula depends upon analyses of at least two separate crops of crystals.

Twenty-three double salts, all but one of which are believed to be new, and 14 triple salts are to be considered.

The first research that will be mentioned is that of Mr. W. K. Wallbridge, who made experiments with solutions of caesium and ferric thiocyanates. After a thorough investigation he found but one double salt,

$$3CsSCN.Fe(SCN)_3.2H_2O.$$

This may be called caesium ferrisulphocyanide, for it corresponds to the ferricyanides in type, and, moreover, Professor Walden, of Riga, has called attention[1] to the resemblance to the complex cyanides of some double thiocyanates partially investigated by him, probably having the formulas

$$K_4Co(SCN)_6.6H_2O, \qquad K_4Mn(SCN)_6.3H_2O,$$
$$\text{and } K_2Zn(SCN)_4.3H_2O.$$

Krüss and Moraht[2] have described the salt

$$3KSCN.Fe(SCN)_3,$$

and a corresponding ammonium salt. These products were obtained by evaporating practically to dryness solutions of the constituents in the required proportions over sulphuric acid. They are described as exceedingly hygroscopic, so that it was impossible to weigh out samples of them, and the water in them, if any, was not determined. If it were not for their analogy with our caesium salt, which is not hygroscopic, and with Rösler's chromium salts,[3]

[1] Ztschr. anorg. Chem., **23**, 373 (1900).
[2] Ann. Chem. (Liebig), **260**, 206 (1890).
[3] *Ibid.*, **141**, 195 (1867).

$(NH_4)_3Cr(SCN)_6.4H_2O$, $Na_3Cr(SCN)_6.7H_2O$,
$K_3Cr(SCN)_6.4H_2O$, and $Ag_3Cr(SCN)_6$,

the reasons for accepting these products as real chemical compounds would appear insufficient. Krüss and Moraht described also $9KSCN.Fe(SCN)_3.4H_2O$, as well as the ammonium, sodium, and lithium salts corresponding exactly to these, even to the same amount of water. These products also were obtained by evaporating practically to dryness solutions of the constituents in the required proportions. It is true that these investigators say that they recrystallized the products; but in one case at least the product was a hard crust, and their descriptions show that these salts were so hygroscopic that the mother-liquors, if there were any, could have differed but little from the solids. Krüss and Moraht state that the sodium salt, the most satisfactory one of the lot, occurred in crystals of two kinds, rhombohedra and hexagonal prisms. This is good evidence of the presence of a mixture. It seems probable, therefore, that insufficient ground exists for accepting these salts with the extraordinary ratio of 9 : 1. Krüss and Moraht were led to believe in the existence of these salts from the fact that the colors of certain ferric salt solutions deepened until 12 molecules of an alkaline thiocyanate had been added; but this phenomenon may now be explained, to some extent at least, by the effect of mass-action in retarding the ionization of ferric thiocyanate.

Mr. Wallbridge experimented also with caesium-lead and potassium-lead thiocyanates, and I have independently confirmed the composition of two of his salts. We have prepared the compounds

$3CsSCN.Pb(SCN)_2$,
$KSCN.Pb(SCN)_2$,
and $6KSCN.Pb(SCN)_2.2H_2O$.

The finding of two potassium salts and only one caesium compound, while all of them are of different types, is somewhat remarkable, but we have made many unsuccessful efforts to prepare other caesium salts. The compound $KSCN.Pb(SCN)_2$ corresponds to the most common type of lead double halides,

while the other two salts represent new types as far as lead is concerned; in fact, the 6 : 1 salt is without parallel among the established double salts of all kinds, and, on this account, it is of great interest. There is no doubt about the existence of this 6 : 1 salt, for it forms good crystals which are stable in the air and are entirely different in appearance from the constituent salts, and we have prepared and analyzed two entirely independent crops of it.

Mr. H. S. Bristol investigated the combinations of caesium and mercuric thiocyanates, and I have extended the experiments considerably in vainly attempting to prepare other double salts. He found only the two salts,

$$2CsSCN.Hg(SCN)_2.H_2O$$

and

$$CsSCN.Hg(SCN)_2.$$

These compounds correspond in type to known double halides, for instance, $2KCl.HgCl_2.H_2O$ and $CsCl.HgCl_2$; moreover, Fleischer[1] has described the salt $2NH_4SCN.Hg(SCN)_2$, which agrees with the first caesium thiocyanate except in regard to water. The striking result of this investigation is the small number of caesium-mercuric thiocyanates as compared with the chlorides, bromides, and iodides, for all of the latter are known in four or five types, as, for example, $Cs_3HgCl_5$, $Cs_2HgCl_4$, $Cs_2HgCl_3$, $CsHg_2Cl_5$, and $CsHg_5Cl_{11}$.[2]

Mr. C. S. Leavenworth has experimented with mixtures of caesium and manganous thiocyanates with the result that he was able to prepare but one salt,

$$4CsSCN.Mn(SCN)_2,$$

under widely varying conditions. This is evidently caesium manganothiocyanate, analogous to Walden's salt,

$$K_4Mn(SCN)_6.3H_2O,$$

which has been mentioned previously.

Mr. R. T. Roberts has made a careful series of attempts to make a caesium-nickel thiocyanate, but without success, for upon allowing solutions containing the two salts in various proportions to evaporate at ordinary temperatures only indefi-

[1] Ann. Chem. (Liebig), **179**, 225 (1875).
[2] Am. J. Sci., **44**, 221 (1892).

nite mixtures were obtained. In this case the thiocyanates show less tendency to form double salts than the chlorides and bromides, although no caesium-nickel iodide could be made by Campbell,[1] who attempted its preparation in this laboratory several years ago.

Mr. Roberts studied also the results obtained by dissolving cuprous thiocyanate in caesium thiocyanate solutions, and obtained only the salt

$$CsSCN.CuSCN.$$

After many attempts he did not succeed in preparing Thurnauer's[2] salt, 6KSCN.CuSCN, and, while Thurnauer himself was uncertain whether this was a double salt or a mixture, we are convinced that the latter was the case.

I found that silver thiocyanate is much more prolific than the cuprous compound in the formation of double salts with caesium thiocyanate, for in a systematic investigation of the matter I have prepared the salts

$$3CsSCN.AgSCN,$$
$$2CsSCN.AgSCN,$$

and

$$CsSCN.AgSCN.$$

Mr. H. F. Merriam found that three potassium salts,

$$3KSCN.AgSCN,$$
$$2KSCN.AgSCN,$$

and

$$KSCN.AgSCN,$$

could be easily prepared, corresponding exactly in composition with the caesium compounds. The 1 : 1 potassium-silver salt has been previously described by Hull,[3] while Fleischer[4] has prepared the corresponding ammonium salt,

$$NH_4SCN.AgSCN.$$

It should be noticed that whereas only one caesium-cuprous thiocyanate could be prepared, three caesium-cuprous chlorides are known. This is another case where the thiocya-

[1] Am. J. Sci., **48**, 418 (1894).
[2] Ber. d. chem. Ges., **23**, 770 (1890).
[3] Ann. Chem. (Liebig), **76**, 96 (1850).
[4] *Ibid.*, **179**, 232 (1875).

nates show less variety of double salts than the halides. On the other hand, the double thiocyanates of silver show a type, the 3 : 1, which is not known among the chlorides and iodides. This apparent exception is probably due to the fact that the double chlorides, bromides, and iodides of silver have not been thoroughly investigated.

While preparing some triple salts, Mr. Merriam encountered the well-crystallized compound

$$2CsSCN.Ca(SCN)_2.3H_2O.$$

He afterwards prepared the salts

$$2CsSCN.Sr(SCN)_2.4H_2O,$$

and

$$2CsSCN.Mg(SCN)_2.2H_2O.$$

The calcium and strontium salts are of unusual interest, because double halides of the alkali metals with barium, strontium, or calcium have been unknown heretofore.[1] The solubility of these two salts increases from the calcium to the strontium compounds, and, although I have made many attempts to prepare a caesium-barium thiocyanate, no satisfactory product has been obtained.

The magnesium salt, $2CsSCN.Mg(SCN)_2.2H_2O$, is remarkable since it differs in type from all the known double halides of magnesium, which are invariably 1 : 1 salts, usually with 6 molecules of water, *e. g.*, $KCl.MgCl_2.6H_2O$. It is interesting, however, to notice that this double thiocyanate of magnesium agrees exactly with the zinc salt which is to be considered immediately.

I have made a thorough investigation with caesium and zinc thiocyanates, and have obtained only the salt

$$2CsSCN.Zn(SCN)_2.2H_2O.$$

The thiocyanates are here not as prolific as the chlorides and bromides, which yield 3 : 1 and 2 : 1 anhydrous salts. I obtained also the salt

$$Zn(SCN)_2.2AgSCN.$$

[1] A potassium-barium nitrite, $K_2Ba(NO_2)_4.H_2O$, and similar strontium and calcium salts have been prepared by Lang (Jsb., 1862, p. 101). Up to the present time these have been, apparently, the only double salts of any kind with alkali and alkaline earth metals, but I have recently prepared a beautifully crystallized, stable double chloride, $2CsCl.CaCl_2.2H_2O$, which will be described in a future article.

Mr. Merriam and I have prepared the double salts

$$Ba(SCN)_2.2AgSCN.2H_2O,$$
$$Sr(SCN)_2.2AgSCN.2H_2O,$$

and $$Ca(SCN)_2.2AgSCN.2H_2O,$$

which form a striking analogous series.

In attempting to prepare a triple salt with the thiocyanates of caesium, barium, and thallium, I obtained, instead of a triple compound, the interesting double salt,

$$CsSCN.4TlSCN.$$

This salt is remarkable, not only because it belongs to the 1 : 4 type which is unknown among the double halides (although 4 : 1 salts are known with negative metals that are not univalent),[1] but especially because thallium in the thallous state has not been known to show any tendency to enter into complex negative radicals. For example, it is well known that thallous iodide is very insoluble in strong solutions of potassium iodide. Thallous thiocyanate, however, which is considerably soluble in water, especially when hot, dissolves also in hot concentrated solutions of caesium thiocyanate, and the double salt crystallizes out upon cooling. This happens even when a large excess of barium thiocyanate is present in the solution.

The double thiocyanates which we have studied correspond in general to the double halides, and, although two new types appear among them, there is no reason to suppose that these types of double halides will not be prepared in the future. The conclusion that I have previously arrived at,[2] namely, that the valency of the negative metal has little or no influence upon the types of double halides formed by it, appears, therefore, to apply also to the double thiocyanates.

Mr. O. G. Hupfel made the original attempt to prepare caesium-silver thiocyanates, which have been mentioned previously, but, in preparing caesium thiocyanate from caesium carbonate and barium thiocyanate, an excess of the latter salt remained in the product, and when silver thiocyanate was

[1] See This JOURNAL, **26**, 401.
[2] *Ibid.*, **26**, 389.

dissolved in a concentrated solution of this mixture, magnificent crystals were produced upon cooling. These proved to be a triple salt of the curious composition represented by the formula

$$3CsSCN.2AgSCN.Ba(SCN)_2.$$

To Mr. Hupfel belongs the credit of making a very interesting accidental discovery, but he was unable, from lack of time, to study the matter further. I undertook, therefore, to thoroughly investigate the products produced from solutions containing the three constituent salts in widely varying proportions. As a result it was found that this triple salt was formed under very wide limits of conditions. It was shown also that, although the compound is decomposed by much water, it is capable of being recrystallized from about its own weight of that liquid.

Then I prepared the analogous salt,

$$3CsSCN.2CuSCN.Ba(SCN)_2.$$

This is also a beautifully crystallized compound, but it is incapable of being recrystallized without filtration on account of the fact that cuprous thiocyanate is more sparingly soluble than the silver salt in concentrated solutions of the other thiocyanates. I was unsuccessful in attempting to introduce thallous, aurous, and mercurous thiocyanates in the place of the silver and cuprous salts.

Mr. Merriam prepared the strontium salts,

$$3CsSCN.2AgSCN.Sr(SCN)_2,$$

and

$$3CsSCN.2CuSCN.Sr(SCN)_2,$$

which are practically identical in appearance and behavior with the barium compounds.

The four triple salts just mentioned are isomorphous, forming tetragonal crystals with steep pyramids and resembling the mineral apophyllite. It is expected that a description of the crystals will be published elsewhere by Mr. J. C. Blake.

Mr. Merriam prepared a caesium-silver-calcium thiocyanate, which formed beautiful crystals and was capable of being recrystallized from a small quantity of water, but it showed a

form and composition differing from the barium and strontium salts, and corresponded to the formula

$$2CsSCN.2AgSCN.Ca(SCN)_2.2H_2O.$$

Mr. Merriam made also the salt

$$2CsSCN.2AgSCN.Mg(SCN)_2.2H_2O,$$

which can be recrystallized from water and forms coherent masses of small crystals. It is very remarkable that the calcium salt agrees in type with the magnesium rather than with the barium and strontium compounds.

Mr. Leavenworth and I prepared and analyzed the manganese salt,

$$2CsSCN.2AgSCN.Mn(SCN)_2.2H_2O.$$

This salt also can be recrystallized unchanged.

Mr. Roberts and I obtained the salts

$$2CsSCN.2AgSCN.Ni(SCN)_2.2H_2O,$$

and

$$2CsSCN.2CuSCN.Ni(SCN)_2.2H_2O.$$

These two salts are very difficultly soluble in water, and, since much water decomposes them, it is impossible to recrystallize either of them without the use of an excess of soluble thiocyanates.

I have made an elaborate study of the caesium-silver-zinc thiocyanates. In this case, for the first time, more than one triple salt was encountered, and it is remarkable that none of the four salts obtained corresponds in type with those previously mentioned. These compounds are:

$$CsSCN.AgSCN.Zn(SCN)_2.H_2O,$$

$$2CsSCN.AgSCN.Zn(SCN)_2,$$

$$CsSCN.3AgSCN.2Zn(SCN)_2,$$

and

$$CsSCN.4AgSCN.2Zn(SCN)_2.$$

These are all well crystallized salts which are too insoluble to be recrystallized from water without decomposition.

I have prepared also a beautifully crystallized potassium salt,

$$4KSCN.2AgSCN.Ba(SCN)_2.H_2O.$$

It is astonishing that this salt, which can be recrystallized from water, differs from the caesium-silver-barium salt, as well as from all the others.

The fourteen triple salts that have been mentioned belong to seven different types :

| | | |
|---|---|---|
| I. | One salt, | $CsAgZn(SCN)_4.H_2O$. |
| II. | One salt, | $Cs_2AgZn(SCN)_5$. |
| III. | Five salts, corresponding to | $Cs_2Ag_2Ca(SCN)_6.2H_2O$. |
| IV. | Four salts, corresponding to | $Cs_2Ag_2Ba(SCN)_7$. |
| V. | One salt, | $K_4Ag_2Ba(SCN)_8.H_2O$. |
| VI. | One salt, | $CsAg_2Zn_2(SCN)_6$. |
| VII. | One salt, | $CsAg_4Zn_3(SCN)_9$. |

The first of these salts might be considered to be a derivative of $Cs_2Ag(SCN)_4$ by the replacement of two caesium atoms by zinc, but a theory of this kind is inapplicable to most of the other types.

The salt $Cs_2Ag_2Mn(SCN)_6.2H_2O$, belonging to type III., might be regarded as a double manganosulphocyanide, analogous to $K_2Na_2Fe(CN)_6.8H_2O$ and $K_2BaFe(CN)_6.3H_2O$, but such a view does not apply to the other types.

The view that these triple salts are compounds of two double salts is also untenable, as far as most of the types are concerned, unless unknown double salts are assumed, although the first salt might be supposed to be composed of

$$Cs_2Zn(SCN)_4 \quad \text{and} \quad Ag_2Zn(SCN)_4,$$

water of crystallization being left out of consideration.

It does not appear that the water of crystallization present in three of the types bears any relation to their composition in replacing other constituents, although it might be assumed that $H_2O$ in I., or $2H_2O$ in III., took the place of one CsSCN in II. and IV.

The arguments which have just been advanced indicate that the triple thiocyanates are not derived from double salts in any simple manner, either by substitution or combination. They must be regarded, therefore, as being built up from simple salts and be viewed as molecular combinations of the same nature as double salts, but more complex than the latter.

It may be mentioned that experiments with lead and mercuric thiocyanates have failed to give me any triple salts with caesium and silver thiocyanates, but the amount of work still to be done on triple thiocyanates is very great. No rubidium, ammonium, sodium, or lithium salts have as yet been investigated, nor has any attempt been made to prepare salts with cobalt, cadmium, and several other bivalent metals. Moreover, it is probable that among the cyanides, fluorides, chlorides, bromides, and iodides, as well as the sulphates, thiosulphates, and other oxygen salts, interesting triple compounds will be found. There is no doubt, as will be evident from the examples, to be given presently, of the few triple salts already known, that these compounds are formed with other groups than the two univalent metals and one bivalent metal present in the thiocyanates under consideration.

It is hoped that the future work which has just been outlined, and which will be industriously carried out in this laboratory, may lead to some insight into the laws of complex molecular combination.

In connection with the triple thiocyanates, attention may be called to a few other triple salts which are known. The compounds which may be regarded as double ferrocyanides, or also as triple cyanides, such as $2KCN.Ba(CN)_2.Fe(CN)_2.3H_2O$ (Bunsen), and which have been mentioned previously, are known in considerable variety. Besides these there are combinations of cyanides and other salts, for example, $4KCN.Mn(CN)_2.2KCl$ (Descamps), $4NH_4CN.Fe(CN)_2.2NH_4Cl.3H_2O$ (Bunsen), $4KCN.Fe(CN)_2.3Hg(CN)_2.4H_2O$ (Kane), $3NH_4CN.KCN.Fe(CN)_2.2NH_4Cl$ (Étard and Bémont), $4KCN.Fe(CN)_2.2NaNO_2.2KNO_2$ (Martius).[1] The last two salts appear to be quadruple. Probably the best known triple salts are the nitrites,

$$K_2BaNi(NO_2)_6,$$

and the corresponding strontium and calcium compounds.[2] These salts may be considered as analogous to the ferrocya-

[1] References to these compounds are in Beilstein's "Handbuch."

[2] Laug: Jsb., (1862) p. 101; Hampe: *Ibid.*, (1863), p. 163; Künzel(Erdmann): Fres. Ztschr., **3**, 161; Erdmann: J. prakt. Chem., **97**, 395.

nides, particularly since the double salt $K_4Ni(NO_2)_6$ is known. Walden,[1] of this laboratory, has described the salts $KBr.FeBr_3.2FeBr_3.3H_2O$ and $RbBr.FeBr_3.2FeBr_3.3H_2O$. Many years ago Bonsdorff[2] described the compound $6KCl.CuCl_2.3HgCl_2.2H_2O$, and recently Mr. Merriam, of this laboratory, has prepared it, and by a partial analysis has confirmed Bonsdorff's results. The minerals pachnolite, $NaF.CaF_2.AlF_3.H_2O$, and polyhalite, $K_2SO_4.2CaSO_4.MgSO_4.2H_2O$, are triple salts. The minerals thaumasite, $CaCO_3.CaSiO_3.CaSO_4.15H_2O$, and sulphohalite, $2Na_2SO_4.NaCl.NaF$, are cases of triple salts with different acid radicals, while hanksite, $9Na_2SO_4.2Na_2CO_3.KCl$, has an additional complication in containing two metals, and northuptite, $MgCO_3.Na_2CO_3.NaCl$, is a triple salt with only two metals and two acids.

Enough examples have been given to show that triple salts exist in considerable variety. It seems probable that these compounds and double salts are governed by the same laws, and that a more thorough knowledge of the more complicated substances may be of assistance in explaining the simpler class.

The more important results of these investigations are :

1. The description of numerous double thiocyanates, among which the salts $6KSCN.Pb(SCN)_2$ and $CsSCN.4TlSCN$ present novel types, while the alkali metal salts with strontium and calcium show that the alkaline earth metals enter into complex negative radicals more readily than has been supposed.

2. The conclusion, from the study of several series of salts, that the thiocyanates generally form double salts in smaller variety than the halides.

3. The discovery of the existence of triple thiocyanates of various types, and particularly the preparation of four distinct triple salts from the thiocyanates of caesium, silver, and zinc.

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## II. Caesium-Ferric Thiocyanate.

By William K. Wallbridge.

Caesium thiocyanate was prepared by boiling a solution of

[1] Am. J. Sci., **48**, 289 (1894).
[2] Pogg. Ann., **33**, 81 (1834).

the ammonium salt with the proper quantity of caesium carbonate until no more ammonium carbonate was given off, and crystallizing the product. A solution of the ferric salt was made by mixing solutions of the required proportions of ferric sulphate and barium thiocyanate, and filtering.

Two solutions were used for the experiments. In the first case ferric thiocyanate was added in small quantities at a time to a solution of 50 grams of caesium thiocyanate, while in the other case caesium thiocyanate was gradually added to a solution of 30 grams of ferric thiocyanate, calculated as the anhydrous salt. After each addition the solution was evaporated in the air or over sulphuric acid until crystals formed, or until it was evident that no satisfactory crystals could be obtained. In the solution containing an excess of the caesium salt, the latter crystallized out, in a pure, or nearly pure condition, until about 15 grams of ferric thiocyanate had been added, when a well crystallized double salt was obtained (analysis I.). Another crop (analysis II.) was prepared by evaporating the mother-liquor. No satisfactory crystals were obtained from the solution containing an excess of ferric thiocyanate until about 24 grams of the caesium salt had been added, when a crop of the same salt as that obtained from the other solution was formed (analysis III.).

These experiments indicate that only one caesium-ferric thiocyanate can be prepared. The results show that this salt has a composition corresponding to the formula $Cs_3Fe(SCN)_6.2H_2O$. It crystallizes in dark, opaque, tabular crystals, often about a centimeter in diameter. The crystals have a beautiful bronze luster and are perfectly stable in the air, although they are exceedingly soluble and are formed only in very concentrated solutions. The following analyses were made:

| | Calculated for $Cs_3Fe(SCN)_6.2H_2O$. | Found. I. | II. | III. |
|---|---|---|---|---|
| Cs | 47.56 | 46.77 | .... | .... |
| Fe | 6.67 | 6.97 | .... | 7.71 |
| SCN | 41.48 | 41.39 | 41.27 | 42.48 |
| $H_2O$ | 4.29 | .... | .... | .... |

In these analyses iron was weighed as the oxide after pre-

cipitation with ammonia, caesium was weighed as the normal sulphate, and sulphocyanogen was determined by the usual volumetric method, usually in a separate sample of the salt.

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## III. The Caesium-Lead and Potassium-Lead Thiocyanates.

By W. K. Wallbridge and H. L. Wells.

*3 : 1 Caesium-Lead Thiocyanate*, $Cs_3Pb(SCN)_5$.—Two series of experiments were carried out with caesium thiocyanate and lead thiocyanate. In the first case about 5 grams of the lead salt were dissolved in a hot concentrated solution of 50 grams of the caesium salt. At first, crystals of lead thiocyanate were deposited upon cooling, but after further concentration a double salt was obtained (analysis I. by Wallbridge). Further additions of the lead salt and variations in the concentration failed to give any other double salt. For the second set of experiments 180 grams of caesium thiocyanate and 20 grams of the lead salt were dissolved in water, and, upon concentrating and cooling, a beautiful crop of the double salt was obtained. Another crop was prepared from the mother-liquor by further concentration, and still another after adding 5 grams more of lead thiocyanate (analyses II., III., and IV. by Wells). The results of the analyses are as follows:

| | Calculated for $Cs_3Pb(SCN)_5$. | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|
| Cs | 44.53 | 45.26 | .... | .... | .... |
| Pb | 23.10 | 21.95 | 22.20 | 22.77 | 23.05 |
| SCN | 32.37 | 31.52 | 32.71 | 32.53 | 32.39 |

This salt forms colorless, transparent massive crystals, which are apparently monoclinic in form. Some of the crystals obtained were nearly 1 cm. in diameter. The salt is stable when exposed to the air. It requires the presence of an excess of caesium thiocyanate for its formation, hence it cannot be recrystallized from water unless a part of the lead salt is removed by filtration.

*1 : 1 Potassium-Lead Thiocyanate*, $KPb(SCN)_3$.—When 5 grams of lead thiocyanate were dissolved in a boiling concentrated solution of 30 grams of the potassium salt a crop of

small, brilliant crystals was obtained upon cooling. They were carefully dried on paper, then air-dried (analysis I.). The mother-liquor was diluted slightly, 5 grams more of lead thiocyanate were dissolved in it by heating, and another crop was obtained by cooling (analysis II.). The analyses (by Wallbridge) are as follows:

| | Calculated for $KPb(SCN)_3$. | Found. I. | II. |
|---|---|---|---|
| K | 9.31 | 9.56 | .... |
| Pb | 49.27 | 48.48 | 50.50 |
| SCN | 41.42 | 41.15 | 40.57 |

This salt forms small, brilliant, white crystals, which are usually less than 1 mm. in diameter. It is stable in the air, but is decomposed by water.

*6 : 1 Potassium-Lead Thiocyanate*, $K_6Pb(SCN)_8.2H_2O$.—A crop of this salt was prepared by allowing the mother-liquor from crop II. of the preceding salt to stand for nearly two weeks exposed to the air at the ordinary temperature (analysis I. by Wallbridge). Another crop was prepared by dissolving 50 grams of potassium thiocyanate and 3 grams of the lead salt in a little hot water, and allowing the liquid to evaporate at ordinary temperature for several days (analysis II. by Wells). The analyses, which were made of material which was carefully dried by pressing between filter-papers and then air-dried, are as follows:

| | Calculated for $K_6Pb(SCN)_8.2H_2O$. | Found. I. | II. |
|---|---|---|---|
| K | 24.91 | 24.80 | .... |
| Pb | 21.98 | 22.20 | 22.02 |
| SCN | 49.28 | 49.07 | 49.09 |
| $H_2O$ | 3.82 | 3.50 | .... |

This salt occurs in white, opaque, prismatic crystals which are stable in the air. The crystals usually grow together and form a peculiar net-work at the bottom of the vessel in which they crystallize. Portions of this net-work of considerable size can be readily removed from the liquid. The individual prisms are about 1 mm. in diameter and several millimeters in length.

In analyzing the double salts of lead, the latter metal and

the alkali metals were weighed as sulphates, while sulphocyanogen was determined in separate samples by titration.

Attempts were made to prepare ammonium-lead thiocyanates, but these were entirely without success.

## IV. The Caesium-Mercuric Thiocyanates.

By H. S. Bristol.

*2 : 1 Caesium-Mercuric Thiocyanate*, $Cs_2Hg(SCN)_4.H_2O$.— This salt is formed under a very wide range of conditions by cooling hot solutions of the component salts. The solution may be almost saturated with the caesium salt and contain about 20 parts by weight of the latter to 1 part of the mercuric salt, or the solution may be much more dilute and contain nearly as much of the mercuric as of the caesium salt. Crop I. was made from 160 grams of caesium thiocyanate and 12 grams of mercuric thiocyanate in a volume of about 500 cc.; crop II. from 160 grams caesium thiocyanate, and 24 grams mercuric thiocyanate in a volume of about 1000 cc. Many other crops were prepared, under widely varying conditions, which were identified by closely agreeing determinations of sulphocyanogen. The analyses are as follows:

| | Calculated for $Cs_2Hg(SCN)_4.H_2O$. | Found. I. | II. |
|---|---|---|---|
| Cs | 37.15 | 37.22 | 37.42 |
| Hg | 27.93 | 27.76 | 27.95 |
| SCN | 32.41 | 32.35 | 32.86 |
| $H_2O$ | 2.51 | .... | 2.25 |

This salt forms large, somewhat flattened, white prisms, which often grow together in parallel position. It is rather freely soluble in water, especially upon warming, and it may be recrystallized unchanged. It melts between 168° and 170°.

*1 : 1 Caesium-Mercuric Thiocyanate*, $CsHg(SCN)_3$. — This salt is produced from solutions containing comparatively little caesium thiocyanate, which are nearly saturated with the mercuric salt. A crop thus made gave the following results on analysis:

| | Calculated for $CsHg(SCN)_3$. | Found I. |
|---|---|---|
| Cs | 26.23 | 25.99 |
| Hg | 39.45 | 39.44 |
| SCN | 34.32 | 34.22 |

Three other crops were identified by titrating the sulphocyanogen not combined with mercury, with the following results:

| | Calculated | Found II. | III. | IV. |
|---|---|---|---|---|
| SCN(with Cs) | 11.44 | 11.15 | 11.51 | 11.64 |

This salt forms large colorless crystals which are often of a pyramidal habit and highly modified with faces. It is difficultly soluble, even in hot water.

No indications of the existence of other double salts were obtained, although it is believed that the search for them was very thorough.

In making the analyses of the two salts, mercury was weighed in a Gooch crucible as sulphide, caesium was weighed as normal sulphate, while sulphocyanogen was determined by titration according to Volhard's method. Where the total sulphocyanogen was determined by this method the mercury was always previously removed by the action of hydrogen sulphide in cold, dilute solution. The observation of Cohn[1] that mercuric thiocyanate is not acted upon in this titration was made use of very satisfactorily in determining occasionally the sulphocyanogen combined with caesium.

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## V. Caesium-Manganous Thiocyanate, $Cs_4Mn(SCN)_6$.

By C. S. Leavenworth.

Only one double salt was obtained by systematic experiments with solutions of caesium and manganous thiocyanates. A solution of manganous thiocyanate was prepared by dissolving the carbonate in dilute thiocyanic acid, the latter having been prepared by the action of hydrogen sulphide upon lead thiocyanate suspended in water, and the excess of hydrogen sulphide removed by passing air through the liquid.

To a concentrated solution of the manganous thiocyanate caesium thiocyanate was added a little at a time until, after evaporation, crystals of the double salt were formed upon cooling and standing. Another series of experiments was made by starting with a concentrated solution of caesium thio-

[1] Ber. d. chem. Ges., 34, 3502.

cyanate and gradually adding small quantities of manganous thiocyanate. Two crops were obtained, one of rather small slender prisms, where the salt was deposited rapidly (I.), the other, by slow evaporation, in magnificent massive crystals (II.). The color is pale yellowish-green. The analyses are as follows:

| | Calculated for $Cs_4Mn(SCN)_6$ | Found. I. | II. |
|---|---|---|---|
| Cs | 56.90 | 57.23 | .... |
| Mn | 5.88 | 5.92 | 6.18 |
| SCN | 37.22 | 36.65 | 37.70 |

In making the analyses, manganese was precipitated as the sulphide and thus separated from caesium. The sulphide was dissolved in hydrochloric acid, and the manganese was determined as the pyrophosphate by the familiar method of Gibbs. The caesium was weighed as the sulphate. Sulphocyanogen was determined in a separate portion by the usual volumetric method.

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## VI. Caesium-Cuprous Thiocyanate, $CsCu(SCN)_2$.

By R. T. Roberts.

This double salt is the only one that could be obtained by dissolving cuprous thiocyanate in solutions of the caesium salt and evaporating to crystallization. It is formed in cold saturated solutions of caesium thiocyanate and crystallizes beside the latter, so that it is evident that no double salt containing a greater proportion of the caesium salt can be prepared. It forms also in solutions that are not quite saturated with caesium thiocyanate, but upon diluting such solutions slightly cuprous thiocyanate precipitates.

The salt forms brilliant colorless prisms, sometimes occurring in massive groups in parallel position 4 or 5 cm. long, and 1 or 2 cm. thick. It is stable in the air, but is decomposed by water with separation of cuprous thiocyanate.

The following analyses are of different crops made under conditions which varied as much as possible. The last crop was made and analyzed by Prof. Wells.

| | Calculated for $CsCu(SCN)_2$ | Found. I. | II. | III. | IV. | V. |
|---|---|---|---|---|---|---|
| CsSCN | 61.13 | 60.50 | 60.41 | 60.71 | 61.13 | 61.69 |
| CuSCN | 38.87 | 38.69 | 38.53 | 38.89 | .... | 38.47 |

Cuprous thiocyanate was determined by treating the salt with water and weighing the precipitate in a Gooch filter, while caesium thiocyanate was determined by titrating the filtrate with decinormal silver nitrate, according to Volhard's method.

Attempts to prepare potassium-cuprous and ammonium-cuprous thiocyanates were without success.

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## VII. The Caesium-Silver Thiocyanates.

By H. L. Wells.

*The 3 : 1 Salt*, $Cs_3Ag(SCN)_4$.—To a nearly saturated solution of 50 grams of caesium thiocyanate the silver salt was added in small portions and dissolved by heating. After 10 grams of the latter had been used a double salt (I.) was formed upon cooling and standing for a few hours. Another crop (II.) was obtained by dissolving 2 grams more of silver thiocyanate in the mother-liquor from the first. It forms very large, transparent, colorless crystals which are stable in the air, and have an octahedral aspect, but are evidently not isometric in form. Crystals a centimeter or more in diameter are easily grown. The following analyses were made:

| | Calculated for $Cs_3Ag(SCN)_4$. | Found. I. | II. |
|---|---|---|---|
| CsSCN | 77.54 | 77.65 | 77.52 |
| AgSCN | 22.46 | 22.39 | 22.34 |

*The 2 : 1 Salt*, $Cs_2Ag(SCN)_3$.—The addition of silver thiocyanate was continued, and when 17 grams in all had been used another salt made its appearance (I.), and another crop of this (II.) was prepared by dissolving 5 grams more of the silver salt in the mother-liquor from the first. Owing to the removal of samples of the double salts for analysis and for specimens, the conditions under which this salt is formed cannot be given very exactly. It forms brilliant, transparent, colorless prisms, sometimes 2 or 3 mm. thick and a centi-

meter or more in length, and it is stable upon exposure to the air. The analyses are as follows:

| | Calculated for $Cs_2Ag(SCN)_3$. | Found. I. | II. |
|---|---|---|---|
| CsSCN | 69.71 | 70.08 | 69.91 |
| AgSCN | 30.29 | 29.71 | .... |

*The 1 : 1 Salt*, $CsAg(SCN)_2$.—The additions of silver thiocyanate were continued with the result that a heavy, syrupy liquid was obtained which for many days refused to deposit crystals. The solution was evidently supersaturated, for when at last some crystals formed and they had been dried on paper the laboratory atmosphere became impregnated to such an extent that no further difficulty was experienced in obtaining crystals from the solution. Two crops were obtained after about 36 grams of silver thiocyanate had been added altogether. The removal of previous crops had doubtless caused the loss of more caesium than silver salt from the solution, so that the proportion of silver salt present was considerably greater than that represented by the quantity added to the original 50 grams of caesium thiocyanate. It appears, therefore, that the two salts must have been present in nearly the required proportion to form this 1 : 1 salt. This double salt forms prismatic crystals of about the same size as the 2 : 1 salt, but they are more flattened and have a higher adamantine luster than the latter. The following analyses were made of two separate crops:

| | Calculated for $CsAg(SCN)_2$. | Found. I. | II. |
|---|---|---|---|
| CsSCN | 53.50 | 54.07 | 53.38 |
| AgSCN | 46.50 | 46.29 | .... |

The analyses were made by treating the substance with a liberal amount of water, collecting and weighing the silver thiocyanate in a Gooch crucible, and titrating the filtrate by Volhard's method. In cases where caesium thiocyanate alone was determined, the titration was made without filtering.

*Caesium Thiocyanate.*—This salt, which apparently has not been described, resembles the potassium compound in the appearance of its crystals. It crystallizes without water. A sample dried on paper gave 29.84 per cent. of SCN, while an-

other sample air-dried gave 30.27 per cent.; calculated for CsSCN, 30.36 per cent. The salt is exceedingly soluble in water, but it is stable in the air, except in very damp, hot weather, when it shows signs of deliquescence. For the work described in the present series of articles it was usually prepared from caesium carbonate and ammonium thiocyanate, but barium thiocyanate and caesium carbonate were also used.

## VIII. The Potassium-Silver Thiocyanates.

By H. F. Merriam.

*The 3 : 1 Salt*, 3KSCN.AgSCN.—This compound was produced from concentrated solutions of about 50 grams of potassium thiocyanate and 15 grams of the silver salt. It forms beautiful, large, transparent, stout prisms which, after drying, gradually become opaque upon standing. This change is not due to loss of water, but depends upon some alteration in crystallization, possibly upon a splitting of the compound into one of the other double salts and potassium thiocyanate. The following analyses were made of two crops of transparent crystals and a sample (III.) which had become opaque by standing:

| | Calculated for $K_3Ag(SCN)_4$. | Found. I. | II. | III. |
|---|---|---|---|---|
| K | 25.65 | 25.80 | .... | .... |
| AgSCN | 36.30 | 35.83 | 36.42 | .... |
| Soluble SCN | 38.05 | 38.28 | 37.59 | 38.22 |

*The 2 : 1 Salt*, 2KSCN.AgSCN.—This was obtained from concentrated aqueous solutions of about 50 grams of potassium thiocyanate and 28 grams of the silver salt. It forms magnificent, large, transparent crystals, which are perfectly stable in the air. The following analyses were obtained with three crops of the salt:

| | Calculated for $K_2Ag(SCN)_3$. | Found. I. | II. | III. |
|---|---|---|---|---|
| K | 21.71 | 21.72 | .... | .... |
| AgSCN | 46.08 | .... | 46.45 | .... |
| Soluble SCN | 32.21 | 32.62 | 32.33 | 32.24 |

*The 1 : 1 Salt*, KSCN.AgSCN.—A crop of this salt was prepared by adding 5 grams of silver thiocyanate to the mother-

liquor from the preceding salt. It crystallizes in very thin, diamond-shaped plates, which by slow growth sometimes attain a diameter of about a centimeter. The following analyses were made:

| | Calculated for $KAg(SCN)_2$. | Found. I. | II. |
|---|---|---|---|
| K | 14.86 | 14.88 | .... |
| AgSCN | 63.10 | 62.38 | .... |
| Soluble SCN | 22.04 | 22.15 | 22.08 |

The analytical methods were the same as those used for the caesium salts, and were mentioned in the preceding article.

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## IX. The Caesium-Calcium, Caesium-Strontium, and Caesium-Magnesium Thiocyanates.

By H. F. Merriam.

*The Calcium Salt*, $2CsSCN.Ca(SCN)_2.3H_2O$.—This was prepared by dissolving about equal weights of the two simple salts in very little water, and concentrating if necessary until the double salt appeared upon standing. The solution has a great tendency to remain in a supersaturated condition and to yield finally very small crystals, but by "seeding," good-sized crystals were grown. The salt forms colorless, transparent prisms which are stable in the air. The following analyses were made of separate crops:

| | Calculated for $Cs_2Ca(SCN)_4.3H_2O$. | Found. I. | II. |
|---|---|---|---|
| Cs | 44.94 | .... | 45.23 |
| Ca | 6.75 | 6.83 | .... |
| SCN | 39.19 | 38.96 | 39.19 |
| $H_2O$ | 9.12 | .... | .... |

The fact may be mentioned here that crystallized calcium thiocyanate has four molecules of water of crystallization instead of three as found by Meitzendorff.[1] The salt, which crystallizes in long prisms, is very hygroscopic. Samples of it were dried over sulphuric acid until the fragments just began to grow opaque on the edges; then sulphocyanogen determinations were made with the following results:

[1] Pogg. Ann., 56, 63 (1842).

| | Calculated for $Ca(SCN)_2.4H_2O$. | Found. |
|---|---|---|
| SCN | 50.87 | 50.63, 51.29, 50.56, 50.36, 50.69 |

The salt becomes opaque over sulphuric acid and changes to $Ca(SCN)_2.2H_2O$, as is shown by the following analyses:

| | | Found | |
|---|---|---|---|
| | Calculated for $Ca(SCN)_2.2H_2O$. | after drying 4 days. | after drying 10 days. |
| SCN | 60.41 | 60.44 | 60.16 |

It is interesting to notice that the crystallized calcium thiocyanate has the same amount of water as the magnesium salt, $Mg(SCN)_2.4H_2O$, while it does not correspond to the salts $Ba(SCN)_2.3H_2O$ and $Sr(SCN)_2.3H_2O$. Some triple thiocyanates which will be described subsequently also show agreements between the calcium and magnesium compounds with lack of analogy between the calcium and the strontium and barium salts.

*The Strontium Salt*, $2CsSCN.Sr(SCN)_2.4H_2O$.—This was prepared by concentrating a solution of equal weights of the two thiocyanates until crystals were formed on cooling, and also by evaporating such a solution in a desiccator. It forms colorless, transparent crystals which are prismatic in habit and often form large compound groups of these crystals in parallel position. All the faces of the crystals appear to be rectangular. The following analyses were made of separate crops:

| | Calculated for $Cs_2Sr(SCN)_4.4H_2O$. | Found. I. | II. |
|---|---|---|---|
| Cs | 40.45 | 40.06 | .... |
| Sr | 13.32 | .... | 13.78 |
| SCN | 35.27 | 35.31 | 35.40 |
| $H_2O$ | 10.96 | .... | .... |

*The Magnesium Salt*, $2CsSCN.Mg(SCN)_2.2H_2O$. — This compound was prepared by slow evaporation in a desiccator of a solution containing 40 grams of caesium thiocyanate and the same quantity of magnesium thiocyanate. It forms magnificent, clear, colorless crystals which are hygroscopic. Two crops gave the following results upon analysis:

| | Calculated for $Cs_2Mg(SCN)_4.2H_2O$. | Found. I. | II. |
|---|---|---|---|
| Cs | 47.63 | .... | ... |
| Mg | 4.37 | 4.59 | .... |
| SCN | 41.55 | 41.45 | 41.50 |
| $H_2O$ | 6.45 | .... | .... |

## X. The Caesium-Zinc and Silver-Zinc Thiocyanates.

By H. L. Wells.

*Caesium-Zinc Thiocyanate*, $Cs_2Zn(SCN)_4.2H_2O$.—This is the only double salt that could be produced under widely varying conditions. It was formed from solutions containing caesium and zinc thiocyanates in the molecular ratios 8 : 1, 4 : 1, 2 : 1, 1 : 1, and 1 : 2. The two crops analyzed were prepared under conditions represented by the first and last ratios. It is evident that the salt may be recrystallized from water. It forms large pyramidal groups of small colorless crystals; it is moderately soluble in water and is stable on exposure to the air. The analyses are as follows:

| | Calculated for $Cs_2Zn(SCN)_4.2H_2O$. | Found. I. | II. |
|---|---|---|---|
| Cs | 44.41 | .... | .... |
| Zn | 10.84 | 10.34 | 11.36 |
| SCN | 38.74 | 37.86 | 38.92 |
| $H_2O$ | 6.01 | .... | .... |

The analyses show some variations, which are due to the presence of a large excess of caesium salt in the first case, and of zinc salt in the second case, in the solutions from which the crops were crystallized.

It may be mentioned that the zinc thiocyanate used was prepared in solution by the exact reaction of barium thiocyanate and zinc sulphate. We attempted to prepare it by boiling ammonium thiocyanate solution with zinc oxide, but this method was unsatisfactory on account of the obstinate retention of considerable quantities of ammonium compounds by the liquid. No crystals of zinc thiocyanate could be prepared by evaporating its solution over sulphuric acid or in the air at the ordinary temperature, but a white efflorescence was obtained, which, when apparently perfectly air-dry, gave 52.4

per cent. of SCN. This corresponds nearly to $Zn(SCN)_2.2H_2O$ which requires 53.46 per cent. Meitzendorff[1] described zinc thiocyanate, crystallized from alcohol, as anhydrous. He mentioned the efflorescence of its solutions, but apparently did not analyze the product.

*Zinc-Silver Thiocyanate*, $ZnAg_2(SCN)_4$, was prepared by dissolving 2.5 grams of silver thiocyanate in a very concentrated solution containing about 85 grams of zinc thiocyanate, calculated as the anhydrous salt. The solution takes place with difficulty, apparently on account of the insolubility of the double salt, the latter being precipitated upon slightly diluting the concentrated solution. Two crops prepared by cooling at considerably different degrees of concentration gave the following results upon analysis:

| | Calculated for $ZnAg_2(SCN)_4$. | Found. I. | Found. II. |
|---|---|---|---|
| Zn | 12.74 | .... | .... |
| AgSCN | 64.67 | 63.72 | 64.02 |
| Soluble SCN | 22.59 | 22.88 | 23.03 |

The salt forms very small, brilliant, colorless, prismatic crystals which are stable in the air, and which retain their transparency when treated with cold water, but become opaque with hot water, and are completely decomposed when the water is boiled for some time.

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## XI. Barium-Silver, Strontium-Silver, and Calcium-Silver Thiocyanates.

By H. L. Wells and H. F. Merriam.

Only one double salt could be prepared in each of these cases by dissolving silver thiocyanate in concentrated solutions of the other thiocyanates. The salts crystallize well, forming colorless prisms in the cases of the barium and calcium compounds, and plates in the case of the strontium salt, all of which are stable in the air. The three compounds are analogous in composition.

*Barium-Silver Thiocyanate*, $Ba(SCN)_2.2AgSCN.2H_2O$, was formed in very concentrated solutions containing about 50

[1] Pogg. Ann., 56, 74 (1842).

grams of barium thiocyanate, and 40 grams of silver thiocyanate. At first the solution remained supersaturated for several days, although it was very dense and syrupy, but after crystals had once been obtained there was no difficulty in obtaining more of them by impregnating the solution. Two crops were analyzed (by Wells):

| | Calculated for $BaAg_2(SCN)_4.2H_2O$. | Found. I. | Found. II. |
|---|---|---|---|
| Ba | 22.11 | .... | .... |
| AgSCN | 53.43 | 52.70 | 52.90 |
| Soluble SCN | 18.67 | 18.69 | 18.73 |
| $H_2O$ | 5.79 | .... | .... |

*The Strontium-Silver Salt*, $Sr(SCN)_2.2AgSCN.2H_2O$, was formed when 15 grams of silver thiocyanate were dissolved in a concentrated solution of 45 grams of strontium thiocyanate, and also when larger quantities of the silver salt were used. Two crops were analyzed (by Merriam):

| | Calculated for $SrAg_2(SCN)_4.2H_2O$. | Found. I. | Found. II. |
|---|---|---|---|
| Sr | 15.32 | 15.33 | .... |
| AgSCN | 58.09 | 57.36 | .... |
| Soluble SCN | 20.29 | 20.42 | 20.52 |
| $H_2O$ | 6.30 | .... | .... |

*The Calcium Salt*, $Ca(SCN)_2.2AgSCN.2H_2O$, was formed after 15 grams of silver thiocyanate had been dissolved in a concentrated solution of 50 grams of calcium thiocyanate, and also when larger quantities of the silver salt were used. Analyses of two crops were made (by Merriam):

| | Calculated for $CaAg_2(SCN)_4.2H_2O$. | Found. I. | Found. II. |
|---|---|---|---|
| Ca | 7.63 | 7.96 | .... |
| AgSCN | 63.36 | 61.72 | 61.79 |
| Soluble SCN | 22.14 | 22.72 | 22.63 |
| $H_2O$ | 6.87 | .... | .... |

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## XII. Caesium-Thallous Thiocyanate, $CsTl_4(SCN)_5$.

By H. L. Wells.

In attempting to prepare a caesium-thallous-barium triple salt, this compound (I.) was obtained by cooling a very concentrated solution containing about 5 grams of thallous thio-

cyanate, 23 grams of barium thiocyanate and 8 grams of caesium thiocyanate. Another crop (II.) was prepared by adding 1 gram of thallous thiocyanate and 7 grams of caesium thiocyanate to the mother-liquor, dissolving by heating, diluting considerably and cooling. The compound forms very small fern-like growths of crystals, which apparently branch at right angles. It has a faint yellow color upon drying, and it is stable in the air. The product is entirely different in appearance from the thin scales of thallous thiocyanate which separate upon cooling hot aqueous solutions of that salt. The results of the analyses are as follows :

| | Calculated for $CsSCN.4TlSCN$. | Found. I. | Found. II. |
|---|---|---|---|
| Cs | 10.73 | 11.09 | 10.22 |
| Tl | 65.86 | 62.69 | 65.28 |
| SCN | 23.41 | 24.10 | 23.14 |
| Ba | .... | 1.63 | 0.40 |

It is to be noticed that crop I., formed in a very concentrated solution of a large amount of barium thiocyanate, was contaminated to a considerable extent with that salt; but if the analysis is corrected for the amount of that salt shown to be present by the barium determination, it becomes very satisfactory. In the other case, where a more dilute solution of barium thiocyanate was used, there was very little contamination. The formation of the double salt was observed in the absence of barium thiocyanate, but it was not considered necessary to analyze this product.

The analyses were made by titrating the sulphocyanogen in separate portions, then treating another sample with aqua regia, evaporating to dryness, taking up with water and a little sulphuric acid, and filtering off and weighing the barium sulphate; then concentrating the filtrate, adding a liberal amount of hydriodic acid and decolorizing with sulphurous acid, adding an equal volume of alcohol, cooling, filtering the thallous iodide on a Gooch filter and washing it with dilute alcohol; then evaporating the filtrate to dryness to remove hydriodic acid, precipitating the caesium as caesium platinic chloride in the presence of dilute alcohol and hydrochloric acid, and weighing the precipitate on a Gooch filter.

## XIII. Caesium-Silver-Barium Thiocyanate, $Cs_3BaAg_3(SCN)_7$.

By O. G. Hupfel and H. L. Wells.

This triple salt was first prepared accidentally under conditions which are not accurately known (analysis I., by Hupfel). Four solutions were then made up hot, containing the following quantities of the salts:

| | No. 1. Grams. | No. 2. Grams. | No. 3. Grams. | No. 4. Grams. |
|---|---|---|---|---|
| CsSCN | 50 | 40 | 20 | 10 |
| $Ba(SCN)_2.3H_2O$ | 10 | 20 | 40 | 50 |
| AgSCN | 8 | 8 | 8 | 8 |

Upon cooling and standing, after proper concentration, all these solutions gave the same triple salt in massive groups of colorless crystals in parallel position. Analysis II. was from No. 1, III. was from No. 4. Upon recrystallizing these products from small amounts of hot water very large, transparent crystals were obtained, which were usually not compound. The crystals are tetragonal, with steep pyramids, resembling the mineral apophyllite, and such magnificent and perfect crystals as these are seldom seen. The substance is perfectly stable upon exposure to the air, but it is readily decomposed by water.

After the above experiments had been made, silver thiocyanate was added to Nos. 1 and 4, eight grams at a time, in order to see if any other triple salt could be produced, but after each addition, up to the point of practical saturation, when 40 grams altogether of the silver salt had been added in each case, the same triple salt was formed. In the course of these experiments it became necessary to add 10 grams more of caesium thiocyanate to No. 4, because the double salt $BaAg_2(SCN)_4.2H_2O$ began to be deposited. The double salt CsSCN.AgSCN was finally formed in No. 1. The analyses are as follows:

| | Calculated for $Cs_3BaAg_3(SCN)_7$. | Found. I. | II. | III. |
|---|---|---|---|---|
| Cs | 34.44 | .... | 33.30 | 33.78 |
| Ba | 11.86 | 11.35 | 11.75 | 12.86 |
| AgSCN | 28.66 | 28.50 | 28.22 | 27.45 |
| Soluble SCN | 25.04 | 25.02 | 25.06 | 25.25 |

Several other crops were identified by sulphocyanogen determinations, but it seems unnecessary to give these results. The analytical methods used here were the same as those which have been mentioned in connection with the double salts; hence they need not be described in this place.

A determination of the solubility of the compound in water was made by analyzing the mother-liquor after recrystallizing the salt three times. The liquid, which was perfectly clear, had stood in contact with the crystals for several days at the laboratory temperature, and had been frequently agitated. Two determinations gave 12.0 and 11.96 per cent. of SCN, corresponding to 48.0 and 47.8 per cent. of the salt. The temperature of saturation was about 19°. At this temperature, therefore, 100 parts of water dissolve about 92 parts of the triple salt.

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## XIV. Caesium-Cuprous-Barium Thiocyanate, $Cs_2BaCu_2(SCN)_7$.

By H. L. Wells.

In investigating this salt the following solutions were prepared, hot and concentrated, and allowed to cool:

| | No. 1. Grams. | No. 2. Grams. | No. 3. Grams. | No. 4. Grams. |
|---|---|---|---|---|
| CsSCN | 50 | 40 | 20 | 10 |
| $Ba(SCN)_2.3H_2O$ | 10 | 20 | 40 | 50 |
| CuSCN | 5 | 5 | 5 | 5 |

This amount of cuprous thiocyanate is nearly the limit of the solubility of this substance in these solutions, as it is far less soluble in solutions of soluble thiocyanates than the silver salt. From No. 1 the previously described double salt, CsSCN.CuSCN, was deposited, containing only a trace of barium; but from Nos. 2, 3 and 4 the triple salt sought was deposited (analyses I., II., and III.). The crystalline habit varied considerably in the three crops, for No. 2 gave mostly large single crystals with prominent pyramidal faces, No. 3 gave large masses of compound crystals which were exactly like the compound crystals of the silver salt, while No. 4 gave very stout, square prisms with only small pyramidal truncations. The analyses are as follows:

| | Calculated for $Cs_3BaCu_2(SCN)_7$. | Found. I. | II. | III. |
|---|---|---|---|---|
| Cs | 37.30 | .... | .... | .... |
| Ba | 12.85 | 12.25 | 13.27 | .... |
| CuSCN | 22.74 | 23.89 | 22.30 | 22.55 |
| Soluble SCN | 27.11 | 26.32 | 27.32 | 27.27 |

The salt forms colorless, transparent crystals which are similar in all respects to the corresponding silver salt. It cannot be recrystallized from water, however, on account of the sparing solubility of cuprous thiocyanate in solutions of the other salts. It is stable in the air, and readily decomposed by water.

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## XV. Caesium-Silver-Strontium and Caesium-Cuprous-Strontium Thiocyanates.

By H. F. Merriam.

These salts, $Cs_3SrAg_4(SCN)_7$ and $Cs_3SrCu_4(SCN)_7$, closely resemble the barium salts in every respect, so that a description of their physical properties may be omitted.

The silver salt was prepared from solutions containing the following quantities of the constituent salts:

| | I. Grams. | II. Grams. | III. Grams. |
|---|---|---|---|
| CsSCN | 45 | 30 | 10 |
| $Sr(SCN)_2.3H_2O$ | 23 | 30 | 50 |
| AgSCN | 15 | 15 | 15 |

It was also prepared by recrystallization from a small quantity of water. The following analyses were made:

| | Calculated for $Cs_3SrAg_2(SCN)_7$. | Found. I. | II. | III. |
|---|---|---|---|---|
| Cs | 35.99 | .... | .... | .... |
| Sr | 7.90 | 8.14 | .... | .... |
| AgSCN | 29.95 | 29.41 | .... | .... |
| Soluble SCN | 26.16 | 26.24 | 26.15 | 26.25 |

The cuprous salt was prepared by dissolving 5 grams of cuprous thiocyanate in a saturated solution of 30 grams of caesium thiocyanate and 30 grams of strontium thiocyanate. Two crops gave the following analyses:

| | Calculated for $Cs_2SrCu_2(SCN)_7$. | Found. I. | II. |
|---|---|---|---|
| Cs | 39.12 | .... | .... |
| Sr | 8.59 | 8.72 | .... |
| CuSCN | 23.85 | 24.17 | .... |
| Soluble SCN | 28.44 | 28.53 | 28.48 |

## XVI. The Caesium-Silver-Calcium, and the Caesium-Silver-Magnesium Thiocyanates.

By H. F. Merriam.

These two triple salts, $Cs_2CaAg_2(SCN)_6.2H_2O$ and $Cs_2MgAg_2(SCN)_6.2H_2O$, are capable of being recrystallized from water. They both form colorless, transparent crystals, those of the calcium salt being very large, while those of the magnesium compound are very small. The magnesium salt is evidently considerably less soluble in water and in the saline solutions than is the calcium salt, while the latter apparently has about the same degree of solubility as the previously described strontium and barium salts containing caesium and silver. It is not known whether the analogous salts under consideration are isomorphous or not.

The calcium compound was deposited by cooling and allowing to stand concentrated solutions containing the following mixtures:

| | I. Grams. | II. Grams. | III. Grams. |
|---|---|---|---|
| CsSCN | 50 | 30 | 20 |
| $Ca(SCN)_2.4H_2O$ | 20 | 30 | 50 |
| AgSCN | 45 | 15 | 25 |

Another crop, IV, was prepared by recrystallization from a small quantity of water. The analyses are as follows:

| | Calculated for $Cs_2CaAg_2(SCN)_6.2H_2O$. | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|
| Cs | 29.36 | .... | .... | .... | .... |
| Ca | 4.43 | 4.61 | 4.58 | .... | .... |
| AgSCN | 36.64 | 35.80 | 36.21 | 35.97 | .... |
| Soluble SCN | 25.60 | 25.90 | 25.70 | 25.95 | 25.59 |
| $H_2O$ | 3.97 | .... | .... | .... | .... |

The magnesium salt was deposited from a solution containing 38 grams of caesium thiocyanate, 21 grams of magnesium

thiocyanate, and 15 grams of silver thiocyanate. Two crops were analyzed as follows:

| | Calculated for $Cs_2MgAg_2(SCN)_6.2H_2O$. | Found. I. | II. |
|---|---|---|---|
| Cs | 29.87 | .... | .... |
| Mg | 2.74 | 2.87 | .... |
| AgSCN | 37.29 | 37.17 | .... |
| Soluble SCN | 26.06 | 26.09 | 26.04 |
| $H_2O$ | 4.04 | .... | .... |

In the case of the magnesium compound no search was made for other triple salts that the same thiocyanates might form.

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## XVII. Caesium-Silver-Manganous Thiocyanate, $Cs_4MnAg_2(SCN)_6.2H_2O$.

By C. S. Leavenworth and H. L. Wells.

A sample of this salt (I.) was prepared by dissolving 20 grams of the salt $Cs_4Mn(SCN)_6$ and 7 grams (two molecular proportions) of silver thiocyanate in a little hot water and cooling. Another crop (II.) was obtained by recrystallizing the first sample from a small quantity of hot water. The results of the analyses (I. by Leavenworth, and II. by Wells) are as follows:

| | Calculated for $Cs_4MnAg_2(SCN)_6.2H_2O$. | Found. I. | II. |
|---|---|---|---|
| Cs | 28.88 | 28.06 | 28.94 |
| Mn | 5.97 | 6.15 | .... |
| AgSCN | 36.05 | 35.94 | 36.20 |
| Soluble SCN | 25.19 | 25.15 | 25.10 |
| $H_2O$ | 3.91 | .... | .... |

The salt forms very slender needles, having a faint greenish tint, which are stable in the air. Like the magnesium salt, it is rather sparingly soluble.

No search was made for other triple salts in this case, for the work with the analogous calcium salt, where only one was found, made the existence of others here seem improbable, and the results with the triple salts of zinc had not yet been obtained when this investigation was carried out.

## XVIII. The Caesium-Silver-Nickel and the Caesium-Cuprous-Nickel Thiocyanates.

By R. T. Roberts and H. L. Wells.

These two salts, $Cs_2NiAg_2(SCN)_6.2H_2O$ and $Cs_2NiCu_2(SCN)_6.2H_2O$, are analogous in composition to the calcium, magnesium, and manganese salts, containing caesium and silver, which have been described already, but they are less soluble in water than the other salts, just referred to, so that it is impossible to make clear solutions from them with water alone when the attempt is made to recrystallize them. They form very small crystals which are stable in the air. The silver salt is sapphire-blue, while the cuprous compound is greenish-blue.

The silver salt was prepared by dissolving about 15 grams of silver thiocyanate and 75 grams of caesium thiocyanate in a solution containing 17 grams of nickel thiocyanate by boiling down to a small volume, then filtering hot and cooling. Two crops at different degrees of dilution were obtained from this solution, and the following analyses were made (I. and III. by Roberts, II. by Wells):

| | Calculated for $Cs_2NiAg_2(SCN)_6.2H_2O$. | Found. I. | II. | III. |
|---|---|---|---|---|
| Cs | 28.75 | 28.46 | 29.81 | .... |
| Ni | 6.37 | 6.51 | .... | 6.55 |
| AgSCN | 35.89 | 36.56 | 35.24 | 36.76 |
| Soluble SCN, | 25.09 | 24.89 | 24.92 | 25.00 |
| $H_2O$ | 3.90 | .... | .... | .... |

The cuprous salt was prepared similarly to the silver salt, but even less cuprous thiocyanate can be dissolved in solutions of the other thiocyanates than is the case with the silver compound. Two crops gave the following results (by Roberts):

| | Calculated for $Cs_2NiCu_2(SCN)_6.2H_2O$. | Found. I. | II. |
|---|---|---|---|
| Cs | 31.82 | .... | .... |
| Ni | 7.02 | 6.78 | 6.77 |
| CuSCN | 29.09 | 29.00 | 29.21 |
| Soluble SCN | 27.76 | 27.97 | 27.99 |
| $H_2O$ | 4.31 | .... | .... |

In regard to the analyses of these salts it may be mentioned that complete decomposition by water required long heating, particularly in the case of the silver salt, and that the nickel was determined by electrolysis.

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## XIX. The Caesium-Silver-Zinc Thiocyanates.

By H. L. Wells.

It is very remarkable that while barium, strontium, and calcium, and apparently also magnesium, manganese, and nickel form only one triple thiocyanate with caesium and silver, zinc forms four of these salts. Another curious circumstance is the fact that all of these zinc salts are different in type from any others that we have prepared. The salts to be described are:

$CsZnAg(SCN)_4.H_2O$,
$Cs_2ZnAg(SCN)_5$,
$CsZn_2Ag_3(SCN)_8$,
and $CsZn_2Ag_4(SCN)_9$.

The investigation of these compounds has been very laborious, because two or three of them crystallized in various habits and were not easy to recognize by their appearance, because several of the salts are very sparingly soluble in the saline solutions, so that it was difficult to obtain crops of them of sufficient size for satisfactory analyses, and because in some cases mixtures were frequently deposited in the place of pure crops. However, it is believed that the work has been thoroughly and accurately carried out, that there is no possibility that any salt described has a variable composition or is a mixture, and that there is little probability that any other triple salts can be produced from these three thiocyanates. Large quantities of caesium and zinc thiocyanates have been employed, mixed in widely varying proportions and diluted to various degrees. The work has been done with as many as eight different solutions of these two salts, and experiments have been carried on with them continuously for several months. The amount of silver thiocyanate used was small, for this compound is very sparingly soluble in solutions containing

zinc thiocyanate, because the triple salts, as well as the double salt $ZnAg_2(SCN)_4$, dissolve in them with great difficulty. The usual method of attempting to prepare a triple salt, therefore, was to add to a caesium and zinc thiocyanate solution somewhat more of the silver salt than it would dissolve upon boiling, and to filter while hot. Sometimes a satisfactory product came down upon cooling, but if the product was not suitable for analysis, or if it was a salt which had been sufficiently investigated, it was removed, or dissolved by heating, and the solution was either allowed to stand for a few days at the ordinary temperature, or a new degree of dilution was tried.

The salt $CsZnAg(SCN)_4.H_2O$ is formed in rather concentrated solutions containing not too small an amount of zinc thiocyanate as compared with the caesium salt present. For instance, it was formed from a solution containing about 11 grams of caesium thiocyanate, 43 grams of zinc thiocyanate, and 1.25 grams of silver thiocyanate in a volume of about 100 cc., and also when the liquid was considerably diluted. It was obtained also from a solution of 23 grams of caesium thiocyanate, 11 grams of zinc thiocyanate, and an unknown, small quantity of silver thiocyanate, as well as from a solution intermediate in composition as compared with the two that have been described. The salt is deposited after the solution has cooled, upon standing, generally in small quantity. It usually forms rather slender, flattened crystals having the outline of very acute rhombs, but in several cases much broader rhomb-shaped crystals were observed. The edges of the crystals are somewhat irregular, apparently because they are formed of smaller individuals joined together. The groups are generally not as much as a centimeter in length, and only about one or two millimeters in width where the more slender habit occurs. The crystals are colorless and brilliant before being removed from the liquid, but this salt differs from all the others in losing water upon exposure to the air, thereby becoming opaque and very brittle. The following analyses, each of which represents an entirely distinct crop, were made with samples that had lost their water more

or less completely by being air-dried, or which, in two cases (V. and VI.), had been dried at 100°:

| | Calculated for $CsZnAg(SCN)_4$. | Found. I. | II. | III. | IV. | V. | VI. | VII. |
|---|---|---|---|---|---|---|---|---|
| Cs | 24.70 | .... | .... | .... | 24.34 | .... | .... | .... |
| Zn | 12.15 | 12.29 | .... | .... | 12.38 | .... | .... | .... |
| AgSCN | 30.82 | 28.94 | 29.97 | 29.68 | 29.22 | 28.44 | 29.68 | 29.99 |
| Soluble SCN | 32.33 | 31.93 | 32.71 | 33.04 | 32.50 | 33.47 | 32.42 | 32.60 |

Water was determined in a sample of V. after it had been well dried, but before it had lost its transparency.

| | Calculated for $CsZnAg(SCN)_4.H_2O$. | Found. |
|---|---|---|
| $H_2O$ | 3.24 | 2.67 |

The salt $Cs_3ZnAg(SCN)_5$ is very easily obtained from solutions which contain an excess of caesium thiocyanate as compared with the zinc salt, and which are rather concentrated. It was deposited from a solution containing 46 grams of caesium thiocyanate, 5.4 grams of zinc thiocyanate, and 2.5 grams of silver thiocyanate in a volume of about 125 cc.; also from a solution with 138 grams of caesium thiocyanate, 21.5 grams of zinc thiocyanate, and small quantities of silver thiocyanate at various degrees of dilution up to 900 cc. It usually crystallizes after a solution has become cold, and is very characteristic in its appearance, since it forms very slender, white needles of rectangular section which usually radiate from points in large numbers. A length of 5 cm. or more was observed with these needles, but their diameter is usually less than a millimeter. The needles dry well when pressed between filter-papers, and they are stable in the air. The following analyses were made of entirely distinct crops:

| | Calculated for $Cs_3ZnAg(SCN)_5$. | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|
| Cs | 36.46 | 37.62 | .... | .... | .... |
| Zn | 8.97 | 8.70 | .... | 8.86 | .... |
| AgSCN | 22.76 | 22.44 | 22.33 | 22.37 | 22.49 |
| Soluble SCN | 31.81 | 31.33 | 30.89 | 31.58 | 31.67 |

The salt $CsZn_2Ag_3(SCN)_8$ is formed in solutions of caesium and zinc thiocyanates when they are saturated when hot with silver thiocyanate and cooled, or upon standing at the ordinary temperature when the solutions are too dilute to yield the

two salts that have been described. It apparently makes little difference whether the caesium thiocyanate is in large excess or not. It was formed, for instance, upon cooling a solution containing 138 grams of caesium thiocyanate and 21.5 grams of zinc thiocyanate, which had been saturated hot with silver thiocyanate at a volume of 750 cc., and it was formed in the same solution, upon standing at the ordinary temperature, when the volume was 1200 cc. It was formed also, by standing at ordinary temperature in a solution containing 17 grams of caesium thiocyanate, 16 grams of zinc thiocyanate, and a small quantity of silver thiocyanate in a volume of about 400 cc. The formation of the salt was observed also in many other cases under a wide range of conditions, but usually in quantities too small for analysis. The compound crystallizes most frequently in small, thin, colorless scales which usually have a rhombic (diamond-shaped) or rhomboidal outline. The scales seldom have a diameter as great as 5 mm. Compound crystals of considerably different habit were also observed. The substance is stable upon exposure to the air, and is slowly decomposed by cold water, but more rapidly by hot. The following analyses were made with separate crops:

| | Calculated for $CsZn_2Ag_3(SCN)_8$. | Found. | | | | | |
|---|---|---|---|---|---|---|---|
| | | I. | II. | III. | IV. | V. | VI. |
| Cs | 12.65 | .... | 11.79 | .... | .... | .... | 13.63 |
| Zn | 12.43 | 12.26 | .... | 11.91 | 12.01 | .... | .... |
| AgSCN | 47.35 | 47.10 | 47.39 | 46.34 | 43.84 | .... | 44.06 |
| Soluble SCN | 27.57 | 27.65 | 27.35 | 27.53 | 27.95 | 27.18 | 28.47 |

It is believed that the determination of silver thiocyanate in IV. is erroneous, but the sample was not large enough to allow the determination to be repeated. Analysis VI. also shows considerable variations, although it was made from a very well crystallized and apparently homogeneous crop. The latter was deposited, by long standing, from a solution containing a much greater proportion of zinc thiocyanate than any of the others, *viz.*, 11.5 grams of caesium thiocyanate, 43.4 grams of zinc thiocyanate, and a small, unknown quantity of silver thiocyanate, at a volume of about 300 cc. It seems probable that this sample was contaminated with a little of the salt $CsZnAg(SCN)_4.H_2O$.

The salt $CsZn_2Ag_4(SCN)_9$ has been the cause of much perplexity during this investigation. It was the first well-crystallized triple salt of zinc encountered, and at that time two good crops of it which had been prepared from a solution of a composition not accurately known, were analyzed. When attempts were made afterwards to produce it from solutions containing known quantities of the salts it was not obtained for a long time. Finally, since it was known that the caesium thiocyanate used in the first experiments was contaminated with a considerable amount of ammonium thiocyanate, the latter salt was added to some of the experimental solutions, and from one of these, but not until after many trials, the much-sought salt was produced. It may be possible to prepare this compound in the absence of the ammonium salt, but although it has been found to contain no ammonia, this has not yet been done. A solution from which two crops were obtained at 700 and 800 cc. contained about 92 grams of caesium thiocyanate, 5.5 grams of zinc thiocyanate, 20 grams of ammonium thiocyanate, and small, unknown quantities of silver thiocyanate. The compound is deposited from cold solutions on standing. It forms very brilliant, flattened, colorless crystals, usually less than 1 cm. in length or diameter, which vary greatly in habit, although the individuals of any single crop are usually nearly uniform. The outlines of the crystals may be nearly triangular, almost square, nearly rhombic, or elongated and nearly rectangular. These variations are evidently due to the fact that the crystals are usually built up of smaller individuals which unite in various ways, apparently by twinning. The salt is stable in the air and is slowly decomposed by water. The following analyses represent four crops of crystals:

| | Calculated for $CsZn_2Ag_4(SCN)_9$. | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|
| Cs | 10.92 | .... | 11.55 | .... | .... |
| Zn | 10.74 | 10.75 | 11.44 | 10.29 | 10.46 |
| AgSCN | 54.53 | 53.52 | 54.23 | 53.88 | 54.29 |
| Soluble SCN | 23.81 | 23.63 | 23.21 | 24.07 | 23.86 |

In regard to the analyses of the caesium-zinc-silver salts it may be mentioned that it was found best to boil the water

added to the samples for about half an hour in order to decompose them completely. Soluble SCN was usually determined, without filtration, in a separate sample. Silver thiocyanate was weighed in a Gooch crucible, and where caesium was not to be determined, the zinc was precipitated from the filtrate with sodium carbonate and weighed as the oxide, also in a Gooch crucible. When caesium was to be determined, the zinc was first precipitated as the sulphide, then the caesium was finally determined, sometimes as the normal sulphate and in other cases in the form of the platinum salt.

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## XX. Potassium-Silver-Barium Thiocyanate.

By H. L. Wells.

This salt, $K_4BaAg_2(SCN)_8.H_2O$, was first formed by evaporating over sulphuric acid a solution of about 135 grams of barium thiocyanate, 95 grams of potassium thiocyanate, and 115 grams of silver thiocyanate in a little water. The selection of these quantities of salts was to some extent accidental, but a very good crop of brilliant crystals was obtained forming a coherent layer upon the surface of the dish in which the evaporation took place. The mother-liquor was extremely dense and syrupy, so that it was very difficult to remove it from the crystals by pressing them upon filter-paper, but as the crystals were hard and solid, and stable in the air, this was satisfactorily accomplished (Analysis I.). The mother-liquor was warmed and again placed over sulphuric acid, when in a few days a small number of small crystals began to grow. These were taken out when they had reached a diameter of about 1 cm. and carefully dried with paper (Analysis II. was made from several of these crystals, III. from a single one). When the second mother-liquor was agitated in removing the large crystals, a very large quantity of small crystals was rapidly formed. These were drained by suction, pressed on paper, and then recrystallized by dissolving in water with the aid of heat, filtering, and evaporating over sulphuric acid. An excellent crop of rather small, transparent crystals was thus obtained (Analysis IV.). All the crystals of this salt, which were inspected, were in the form of rectangular pyramids

truncated with rather large, square basal planes. Mr. J. C. Blake has kindly examined the crystals and finds that the pyramidal faces do not correspond to those of the caesium-silver-barium salt, being much less steep. As has been previously mentioned the crystals are brilliant, transparent, and stable in the air. They are exceedingly soluble in small quantities of water, but are decomposed by much of it with precipitation of silver thiocyanate. The analyses are as follows:

| | Calculated for $K_4BaAg_3(SCN)_8.H_2O$. | Found. I. | II. | III. | IV. | |
|---|---|---|---|---|---|---|
| K | 15.79 | .... | .... | .... | 14.78 | 14.73 |
| Ba | 13.85 | 14.55 | 15.15 | .... | 14.69 | 14.71 |
| AgSCN | 33.47 | 33.27 | 33.19 | 33.24 | 33.17 | |
| Soluble SCN | 35.08 | 35.94 | 34.85 | 34.95 | 34.94 | |
| $H_2O$ | 1.81 | .... | .... | .... | .... | |

NEW HAVEN, CONN., July, 1902.

## THE LOWERING OF THE FREEZING-POINT OF AQUEOUS HYDROGEN DIOXIDE PRODUCED BY CERTAIN SALTS AND ACIDS.

BY HARRY C. JONES AND CHARLES G. CARROLL.

A short investigation on the lowering of the freezing-point of aqueous hydrogen dioxide by certain salts has already been carried out in this laboratory.[1] The object of the investigation was to ascertain, if possible, whether hydrogen dioxide has a greater dissociating power than water. This was all the more desirable since Calvert[2] had shown that the dielectric constant of aqueous hydrogen dioxide is greater than that of pure water; and from the Thomson-Nernst hypothesis we must conclude that the solvent with the higher dielectric constant has the greater dissociating power. The attempt was made to measure the dissociation of salts in aqueous hydrogen dioxide by means of the conductivity method, but this was abandoned on account of the decomposition of the dioxide by the metal electrodes. Bredig and Calvert[3] have since pointed out that iron covered with tin can

[1] Jones, Barnes and Hyde: This JOURNAL, **27**, 22 (1902).
[2] Ann. der Phys., **1**, 483.
[3] Ztschr. Elektrochem., **7**, 622; Ztschr. phys. Chem, **38**, 513.

be used as electrodes for measuring the conductivity of solutions of electrolytes in aqueous hydrogen dioxide. This part of the problem has been left to them since we have learned privately from Bredig that he desires to continue work upon this phase of the subject.

The freezing-point method was resorted to as the best means available for measuring the dissociation of electrolytes in aqueous hydrogen dioxide, and Jones, Barnes, and Hyde[1] measured the freezing-point lowering of aqueous hydrogen dioxide produced by potassium chloride, sodium nitrate, and potassium nitrate. They found that the lowering of the freezing-point of aqueous hydrogen dioxide produced by the above-named salts was always less, and in the case of potassium nitrate very much less than the lowering of the freezing-point of pure water. The natural inference from these results would be that aqueous hydrogen dioxide has less dissociating power than pure water, that the presence of the hydrogen dioxide drives back the dissociation of the salt. The lowering of the freezing-point of aqueous hydrogen dioxide is, however, so much less than that of pure water, especially in the case of potassium nitrate, that it would be very difficult to explain the results simply on the assumption of a driving back of the dissociation.

Just before the earlier work in this laboratory was published a paper appeared by Bredig,[2] and one a little later by Calvert,[3] which seemed to furnish us with a rational explanation of the results which we had obtained. Bredig and Calvert made it very probable by the conductivity, freezing-point, and other methods, that the strong alkalies can combine with hydrogen dioxide, forming definite compounds with it. They concluded that hydrogen dioxide is a weak acid.

It seemed probable from our earlier results that salts also can combine with hydrogen dioxide, especially salts like potassium nitrate.

### *Salts.*

The present investigation was undertaken for the purpose

[1] This JOURNAL, **27**, 22 (1902).
[2] Ztschr. Elektrochem., **7**, 622.
[3] Ztschr. phys. Chem., **38**, 513.

of obtaining more data bearing on this point. Some of the earlier measurements with potassium chloride were repeated, and especially those with potassium nitrate, which gave an unexpectedly small lowering of the freezing-point of aqueous hydrogen dioxide. Hydrogen dioxide of two different concentrations was used with potassium nitrate, as will be seen from the following results.

Both of the above-named salts are binary electrolytes, yielding only two ions. It was desirable to study the lowering of the freezing-point of aqueous hydrogen dioxide, as compared with water, which would be produced by a ternary salt. Ammonium sulphate was chosen on account of its high solubility.

The hydrogen dioxide which was used was purified and concentrated by the method already described,[1] and the solutions were prepared by the same general method as that employed in the first investigation. We were especially careful to keep the temperature low while the salt was dissolving in the dioxide, and in every case we determined the concentration of the dioxide after the salt had completely dissolved. In most cases the amount of decomposition was so slight that it could be neglected. Wherever an appreciable decomposition had taken place a corresponding correction in the freezing-point of the pure solvent was introduced.

The strength of the hydrogen dioxide, both before and after the solution of the salt, was determined by titrating with a solution of potassium permanganate of known concentration.

The results which were obtained with the three salts named above are given in the following tables. The first column contains the strength of the solution of the salt, the second the lowering of the freezing-point of the aqueous hydrogen dioxide corrected for the separation of ice. The third is the molecular lowering of the freezing-point of the dioxide. The strength of the dioxide employed is given in percentage.

For the sake of comparison the lowerings of the freezing-point of water produced by the same substances at the same concentrations were determined under exactly the same con-

[1] This JOURNAL, 37, 24 (1902).

ditions as the lowering of the freezing-point of the dioxide. The results for aqueous solutions are also given below:

*Potassium Chloride in Water.*

| Concentration. | Observed F. P. lowering. | Molecular lowering. |
|---|---|---|
| 1.00 | 3°.370 | 3°.370 |
| 0.75 | 2°.521 | 3°.362 |
| 0.50 | 1°.6745 | 3°.349 |
| 0.25 | 0°.838 | 3°.341 |
| 0.20 | ..... | 3°.430 |
| 0.10 | ..... | 3°.469 |

*Potassium Chloride in Hydrogen Dioxide (4.35 per cent).*

| Concentration. | Observed F. P. lowering. | Molecular lowering. |
|---|---|---|
| 1.00 | 2°.996 | 2°.996 |
| 0.50 | 1°.465 | 2°.930 |
| 0.25 | 0°.719 | 2°.876 |
| 0.125 | 0°.3555 | 2°.844 |
| 0.0625 | 0°.182 | 2°.944 |
| 0.03125 | 0°.094 | 3°.008 |

*Potassium Nitrate in Water.*[1]

| Concentration. | Observed F. P. lowering. | Molecular lowering. |
|---|---|---|
| 1.00 | 2°.656 | 2°.656 |
| 0.75 | 2°.107 | 2°.809 |
| 0.50 | 1°.470 | 2°.940 |
| 0.25 | 0°.771 | 3°.084 |

*Potassium Nitrate in Hydrogen Dioxide (4.35 per cent).*

| Concentration. | Observed F. P. lowering. | Molecular lowering. |
|---|---|---|
| 1.00 | 2°.264 | 2°.264 |
| 0.50 | 1°.245 | 2°.490 |
| 0.25 | 0°.651 | 2°.604 |
| 0.125 | 0°.342 | 2°.736 |

*Potassium Nitrate in Hydrogen Dioxide (5.507 per cent).*

| Concentration. | Observed F. P. lowering. | Molecular lowering. |
|---|---|---|
| 1.00 | 2°.156 | 2°.156 |
| 0.50 | 1°.193 | 2°.386 |
| 0.25 | 0°.613 | 2°.452 |
| 0.125 | 0°.320 | 2°.560 |

[1] Jones, Barnes, and Hyde: This JOURNAL, 27, 29.

*Ammonium Sulphate in Water.*

| Concentration. | Observed F. P. lowering. | Molecular lowering. |
|---|---|---|
| 1.00 | 3°.761 | 3°.761 |
| 0.50 | 1°.934 | 3°.868 |
| 0.25 | 1°.026 | 4°.104 |
| 0.20[1] | ..... | 4°.145 |
| 0.10[1] | ..... | 4°.370 |

*Ammonium Sulphate in Hydrogen Dioxide (4.108 per cent).*

| Concentration. | Observed F. P. lowering. | Molecular lowering. |
|---|---|---|
| 1.00 | 3°.203 | 3°.203 |
| 0.50 | 1°.634 | 3°.268 |
| 0.25 | 0°.8545 | 3°.428 |
| 0.125 | 0°.445 | 3°.560 |
| 0.0625 | 0°.233 | 3°.728 |

*Ammonium Sulphate in Hydrogen Dioxide (3.23 per cent).*

| Concentration. | Observed F. P. lowering. | Molecular lowering. |
|---|---|---|
| 1.00 | 3°.203 | 3°.203 |
| 0.50 | 1°.665 | 3°.330 |
| 0.25 | 0°.871 | 3°.484 |
| 0.125 | 0°.454 | 3°.632 |
| 0.0625 | 0°.237 | 3°.792 |

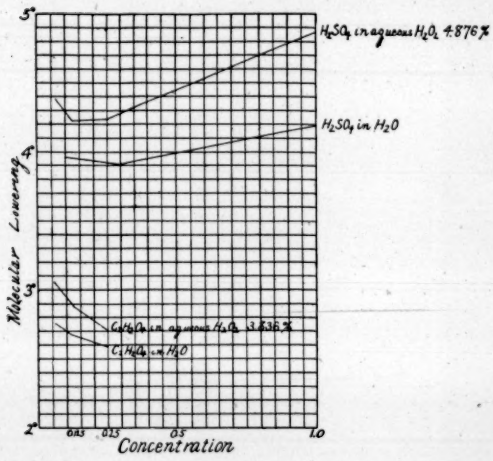
A comparison of the above results with those obtained by Jones, Barnes, and Hyde, will show that the former confirm the latter. The lowering of the freezing-point of aqueous hydrogen dioxide by potassium chloride is much less than the lowering of the freezing-point of water produced by the same salt at the same concentrations.

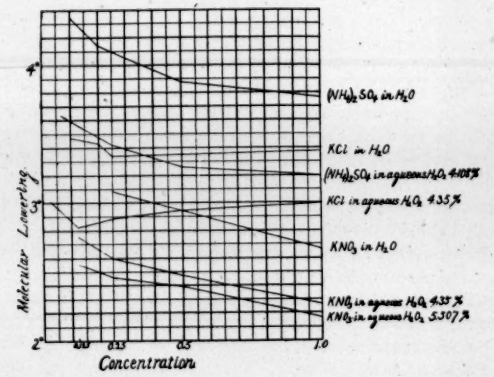
The measurements of the freezing-point lowerings produced by potassium nitrate were repeated with special care, using two concentrations of the dioxide. This seemed desirable on account of the very small values found in the first investigation with this salt. Our results confirm very satisfactorily those of Jones, Barnes, and Hyde.

The conclusion which applies to the above two salts holds also for ammonium sulphate. The lowering of the freezing-point of the dioxide is much less than that of water under the same conditions of concentration of the salt.

The relations between the lowering of the freezing-point of

[1] Jones: This Journal, **19**, 115.


$H_2SO_4$ in aqueous $H_2O_2$ 4·876%
$H_2SO_4$ in $H_2O$
$C_6H_8O_6$ in aqueous $H_2O_2$ 3·636%
$C_6H_8O_6$ in $H_2O$
Molecular Lowering
Concentration
5°
4°
3°
2°
0·13
0·23
0·5
1·0


$(NH_4)_2SO_4$ in $H_2O$
KCl in $H_2O$
$(NH_4)_2SO_4$ in aqueous $H_2O_2$ 4·108%
KCl in aqueous $H_2O_2$ 4·35%
$KNO_3$ in $H_2O$
$KNO_3$ in aqueous $H_2O_2$ 4·33%
$KNO_3$ in aqueous $H_2O_2$ 5·307%
Molecular Lowering
Concentration
4°
3°
2°
0·13
0·23
0·5
1·0

water and of the aqueous solution of the dioxide, as produced by the above-named salts, can be seen best by plotting the two sets of values for each salt in the form of curves. The abscissas are concentrations of the salt in the solvent, the ordinates are molecular lowerings of the freezing-point. The curves for water as the solvent, lie, in every case, well above those in the aqueous dioxide.

From results similar to these Bredig and Calvert concluded that the strong alkalies form compounds with aqueous hydrogen dioxide or, in other words, that hydrogen dioxide in the presence of water is a weak acid.

Our results with the above-named salts can apparently be interpreted in several ways. The dioxide may effect great polymerization of the salt molecules, or may greatly drive back the dissociation of the salt. Both of these explanations seem to us improbable, especially when we consider the results obtained with potassium nitrate. The lowering of the freezing-point of aqueous hydrogen dioxide produced by this salt is so much less than the lowering of the freezing-point of water, that it is difficult to account for the difference on the assumption either of polymerization or a driving back of the dissociation.

The most probable explanation of the above results, all things considered, seems to us to be that there is union between the molecules of the several salts investigated and the molecules of hydrogen dioxide. This is made the more probable by the work of Tanatar,[1] who pointed out the existence of compounds of potassium fluoride and hydrogen dioxide, and also of sodium sulphate and sodium nitrate and the dioxide.

*Acids.*

Having found the above results with salts we next turned our attention to acids, to see whether relations similar to the above existed between the freezing-point lowering of water and of aqueous hydrogen dioxide, produced by them. This was all the more desirable since Bredig and Calvert had already worked with bases and had discovered relations similar to those found by us for salts.

[1] Ztschr. anorg. Chem., 28, 255.

The work carried out thus far with acids is only preliminary. We, however, give the results which we have obtained:

*Sulphuric Acid in Water.*

| Concentration. | Observed F. P. lowering. | Molecular lowering. |
|---|---|---|
| 1.0 | 4°.190 | 4°.190 |
| 0.5 | 2°.030 | 4°.060 |
| 0.3 | 1°.173 | 3°.910 |
| 0.1 | 0°.396 | 3°.960 |

*Sulphuric Acid in Aqueous Hydrogen Dioxide (4.876 per cent).*

| Concentration. | Observed F. P. lowering. | Molecular lowering. |
|---|---|---|
| 1.0 | 4°.859 | 4°.859 |
| 0.5 | 2°.220 | 4°.440 |
| 0.25 | 1°.056 | 4°.244 |
| 0.125 | 0°.528 | 4°.224 |
| 0.0625 | 0°.274 | 4°.384 |

*Oxalic Acid in Water.*

| Concentration. | Observed F. P. lowering. | Molecular lowering. |
|---|---|---|
| 0.25 | 0°.646 | 2°.576 |
| 0.125 | 0°.336 | 2°.688 |
| 0.0625 | 0°.1725 | 2°.760 |

*Oxalic Acid in Aqueous Hydrogen Dioxide (3°.836 per cent).*

| Concentration. | Observed F. P. lowering. | Molecular lowering. |
|---|---|---|
| 0.25 | 0°.680 | 2°.720 |
| 0.125 | 0°.360 | 2°.880 |
| 0.0625 | 0°.204 | 3°.264 |

The results for acids are plotted as curves (Fig. II.), which show clearly that the lowering of the freezing-point of aqueous hydrogen dioxide is considerably greater than that of water. These results would indicate that the acids are dissociated to a greater extent by the dioxide than by water. The data thus far obtained for acids are, however, so meager that no final conclusion can be drawn from them. We propose to repeat the above measurements as well as extend this investigation to a much larger number of substances.

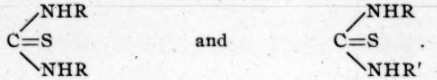
CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
June, 1902.

Contributions from the Chemical Laboratory of the Nebraska Wesleyan University.

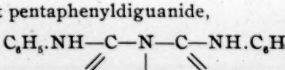
# III.—ON THE AROMATIC GUANIDINES.

By Frederick J. Alway and Frederick W. Viele.

Marckwald[1] has carefully investigated the action of aniline, of *p*-toluidine, and of *o*-toluidine upon diphenylcarbodiimide, and that of aniline and of *o*-toluidine upon di-*o*-tolylcarbodiimide, and less carefully the action of some of these aromatic amines upon mixed carbodiimides such as phenyl-*p*-tolylcarbodiimide, as well as their action upon some of the corresponding thioureas of the general formulæ :



He found that pentaphenyldiguanide,



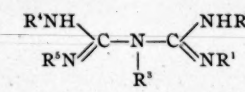
was formed, together with triphenylguanidine, by allowing an alcoholic solution of aniline and diphenylcarbodiimide to stand for a time at the temperature of the room. A great excess of aniline did not prevent the formation of the diguanide. The analogous tetraphenyl-*p*-tolyldiguanide and diphenyl-*p*-tolylguanidine were obtained by the action of *p*-toluidine upon diphenylcarbodiimide. The formation of this diguanide was not proven in the preparation of the guanidine from aniline and phenyl-*p*-tolylcarbodiimide, from *p*-toluidine and diphenylthiourea with lead oxide, or from aniline and phenyl-*p*-tolylthiourea with lead oxide. *o*-Toluidine, unlike aniline and *p*-toluidine, did not react with diphenylcarbodiimide to produce a diguanide as well as a guanidine. Diphenyl-*o*-tolylguanidine was the only product of the reaction. The reaction followed a different course where *o*-tolyl groups were present.

Both phenyldi-*o*-tolylguanidine and tri-*o*-tolylguanidine

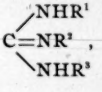
[1] Ann. Chem. (Liebig), **286**, 361.

were formed by the interaction of di-*o*-tolylcarbodiimide and aniline, of phenyl-*o*-tolylcarbodiimide and *o*-toluidine, of di-*o*-tolylthiourea, aniline, and lead oxide, and of phenyl-*o*-tolylthiourea, *o*-toluidine, and lead oxide. The tri-*o*-tolylguanidine was the only compound obtained by the action of *o*-toluidine upon di-*o*-tolylcarbodiimide.

In the hope of finding some relation between the course of the reaction and the structure of the reacting diimide or that of the amine, we have undertaken a thorough investigation of the formation of diguanides and guanidines of the general formulæ:




and

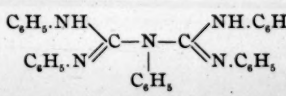



wherein $R^1$, $R^2$, $R^3$, $R^4$, and $R^5$ are all alike, partly alike, or all different.

As this investigation must be discontinued for some time we give below the results of our work up to the present time. *m*-Toluidine is analogous to *p*-toluidine in its action upon diphenylcarbodiimide, yielding a mixture of diphenyl-*m*-tolylguanidine and tetraphenyl-*m*-tolyldiguanide, or the former of these compounds alone, according to the conditions under which the reaction is allowed to take place.

## EXPERIMENTAL.

*Pentaphenyldiguanide,*




.—

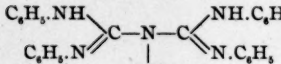
That we might form some idea of the yield of this compound under favorable circumstances, we prepared it according to the method described by Marckwald,[1] as he had kindly informed us in a private communication that he had no record of the yield of the guanidines and the diguanides described in his article to which we refer.

Twelve grams diphenylcarbodiimide (boiling-point 192° at 28 mm.) and 3 grams freshly distilled aniline were mixed to-

[1] *Loc. cit.*

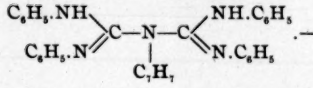
gether with 40 cc. alcohol (90 per cent). After standing a few days at the temperature of the room the mixture had become an almost solid mass. The white, crystalline mass thus obtained was extracted with 330 cc. of warm alcohol (90 per cent) and washed on the filter several times with hot alcohol of the same strength. The dried residue weighed 8 grams. The product thus obtained melted at 157°. (Triphenylguanidine melts at 144° and pentaphenyldiguanide at 160°.) The same compound was obtained by melting 11 grams *β*-diphenylcarbodiimide and adding to this liquid 3 grams aniline. The mixture solidified on cooling to a transparent, glassy mass. After standing for two months it had undergone no change in appearance. It was then melted. The molten substance, on being stirred, changed to a white, crystalline mass. This was treated with 90 per cent alcohol in the same manner as the product obtained in the preceding experiment. The residue in this case weighed only 1.5 grams. The insoluble substance thus obtained was fully identified as pentaphenyldiguanide.

*Tetraphenyl-p-tolyldiguanide*,



.—This compound was obtained by dissolving 7 grams diphenylcarbodiimide and 3.5 grams *p*-toluidine in absolute alcohol and allowing the mixture to stand at the temperature of the room. The crystalline mass, after treatment with excess of boiling 90 per cent alcohol, yielded 1.25 grams of the above compound. This compound seems to be formed in smaller quantity by the action of *p*-toluidine (1 mol.) and lead hydroxide upon diphenylthiourea (1 mol.) in alcoholic solution. An excess of *p*-toluidine does not prevent its formation. When the reaction-product is extracted with 95 per cent alcohol, even the tenth extract gives a white deposit on cooling. This substance was found to be diphenyl-*p*-tolylguanidine and evidently results from the gradual decomposition of the diguanide.

*Tetraphenyl-m-tolyldiguanide,*



.—To 25 grams absolute alcohol we added 5.1 grams *m*-toluidine and 10 grams diphenylcarbodiimide. Within five minutes the temperature had risen 20° to 30°. After four hours a white solid began to separate out. The mixture was stirred frequently during the following ten hours, and at the end of a day and a half was an almost solid, white, crystalline mass. This was warmed with 90 per cent alcohol and repeatedly washed on the filter with boiling alcohol of the same strength. The filtrate contained diphenyl-*m*-tolylguanidine. The white residue weighed 8 grams and melted at 136°. The melting-point was not sharp. Recrystallization from absolute alcohol, from benzene, or solution in benzene and precipitation from this by ligroin did not give a substance with a higher melting-point. The residue consists of pure tetraphenyl-*m*-tolyldiguanide. The base is readily soluble in acetone and benzene, much less soluble in boiling absolute alcohol, and only sparingly soluble in ether, ligroin, cold absolute alcohol, or boiling aqueous alcohol.

| | Calculated for $C_{33}H_{29}N_5$. | Found. |
|---|---|---|
| N | 14.1 | 14.0 |

The hydrochloride was obtained by covering the finely pulverized base with warm alcohol and adding to this mixture an excess of concentrated hydrochloric acid. The clear solution thus obtained was placed in a freezing-mixture of ice and salt and, while kept agitated, an excess of ice-cold water was added in small portions. A white, crystalline precipitate was formed. This was thoroughly washed on the filter with ice-cold water.

| | Calculated for $C_{33}H_{29}N_5.HCl$. | Found. | | |
|---|---|---|---|---|
| | | I. | II. | III. |
| HCl | 6.9 | 6.4 | 6.8 | 6.5 |

By the addition of a dilute aqueous solution of platinic chloride to the solution of the above chloride in dilute alcohol, the chlorplatinate was obtained as a flesh-colored, amorphous pre-

cipitate, which melted at 140° with decomposition. It is readily soluble in alcohol, but insoluble in water.

| | Calculated for $(C_{26}H_{29}N_5)_2H_2PtCl_6$. | Found. |
|---|---|---|
| Pt | 13.9 | 13.9 |

*Diphenyl-m-tolylguanidine*, $C{=}N.C_7H_7$ ($NH.C_6H_5$, $N.H.C_6H_5$). —This compound was obtained, together with the diguanide described above, by the action of *m*-toluidine (1 mol.) upon diphenylcarbodiimide (2 mol.) in the cold. It was the chief product when *p*-toluidine (1 mol.) was mixed with diphenylcarbodiimide (1 mol.) in absolute alcohol, and the mixture allowed to stand at the temperature of the room for several days. At the end of this time a small amount of the diguanide (0.25 gram) had separated out and was removed by filtration. When the mixture (of 1 mol. with 1 mol.) was heated on the water-bath for two hours, no diguanide was obtained, the whole reaction-product being readily soluble in hot, 90 per cent alcohol. Some impurity is, however, present in all the above cases, as the guanidine separated out of the solution very slowly, and in varying amounts, as colorless crystals, which did not possess a sharp melting-point, while the pure guanidine crystallizes readily from aqueous alcohol.

The following was found to be the most satisfactory method of obtaining it in quantity. Diphenylthiourea (1 mol.) was dissolved in the minimum amount of boiling ordinary alcohol, *m*-toluidine (1 mol.) added, and lead hydroxide then added in small portions until the desulphurization was complete. The hot reaction-mixture was filtered under suction and the black residue of lead sulphide boiled with a quantity of alcohol equal to that used in the first case, and the mixture filtered. The two alcoholic solutions were mixed, cooled under the tap, and treated with a quantity of concentrated nitric acid slightly greater than the theoretical amount required. The solution became red and crystals soon began to separate out. After some hours had elapsed the crystals were filtered out, washed with a little cold alcohol, redissolved in this sol-

vent, and boiled with bone-black. On cooling the filtered solution colorless crystals were obtained. After the fourth recrystallization from alcohol the melting-point remained constant at 179°. The base was obtained from the nitrate by treatment with dilute potash, and recrystallization from alcohol. This compound crystallizes in stellate groups of colorless needles that melt at 132°. It is very soluble in hot absolute alcohol and in hot benzene, from both of which it crystallizes on cooling. It is soluble in aqueous alcohol and in ether, but insoluble in water.

| | Calculated for $C_{20}H_{19}N_3$. | Found. |
|---|---|---|
| N | 13.9 | 14.0 |

The *nitrate* is readily obtained by the addition of nitric acid to the alcoholic solution of the base. It forms colorless, hard crystals, which melt with decomposition at 179°, and are readily soluble in hot alcohol, and sparingly soluble in cold alcohol and in water.

| | Calculated for $C_{20}H_{19}N_3.HNO_3$. | Found. I. | II. | III. |
|---|---|---|---|---|
| $HNO_3$ | 17.3 | 17.6 | 17.8 | 17.6 |

The *hydrochloride* was obtained by treating the alcoholic solution of the base with dilute hydrochloric acid. It forms colorless plates that melt at 195°. It is slightly soluble in cold water, and readily soluble in cold alcohol.

| | Calculated for $C_{20}H_{19}N_3.HCl$. | Found. I. | II. |
|---|---|---|---|
| HCl | 10.8 | 11.2 | 11.2 |

The *chlorplatinate* is obtained by the addition of platinic chloride to the solution of the hydrochloride in aqueous alcohol. It forms orange-red leaflets that melt at 237°.

| | Calculated for $(C_{20}H_{19}N_3)_2H_2PtCl_6$. | Found. |
|---|---|---|
| Pt | 19.2 | 19.4 |

UNIVERSITY PLACE,
May, 1902.

# THE DETERMINATION OF PHOSPHORIC ACID BY MEANS OF AMMONIUM PHOSPHOMOLYBDATE.

By Gregory Paul Baxter.

The composition of ammonium phosphomolybdate has received considerable attention with a view to its use, when weighed directly, as a means of determining phosphoric acid. But although it has been shown that under definite conditions the precipitate has, within certain limits, a fixed composition, the effect of varying conditions has never been carefully studied, and the consensus of opinion has been that its composition is too uncertain to warrant its use for the accurate estimation of phosphoric acid.

The formula usually assigned to the ammonium phosphomolybdate is $(NH_4)_3PO_4.12MoO_3$, which contains 3.783 per cent of phosphoric anhydride. That this formula is only an approximation can be seen from the following experimental results:

| | |
|---|---|
| Rammelsberg[1]—Dried at 100° | 3.90 |
| Finkener[2]—Washed with ammonium nitrate and heated to volatilization of the nitrate | 3.794 |
| Gladding[3]—Washed with 1 per cent nitric acid and dried at 105° | 3.76 |

Furthermore, the after treatment of the precipitate is not the only factor which determines its composition. Few substances are so susceptible to the influence of the conditions under which precipitation takes place. Hence it is not at all surprising that the method under discussion has never found favor in the eyes of quantitative analysts.

Most methods of determining phosphoric acid in the presence of bases precipitable by ammonia require preliminary precipitation of the phosphoric acid by molybdic acid. Solution of the ammonium phosphomolybdate in ammonia and double precipitation of the magnesium ammonium phosphate

[1] Ber. d. chem. Ges., 10, 1776.
[2] *Ibid.*, 11, 1638.
[3] J. Am. Chem. Soc., 18, 23.

is troublesome and time-exacting, and, since much manipulation is necessary, correspondingly inexact. Pemberton's volumetric method of solution in standard potassium hydroxide and titration with standard acid is subject to the errors due to loss of ammonia even when N/5 solutions are used, and to the uncertainty of the end-point with phenolphthalein in the presence of ammonium salts. The method of weighing the ammonium phosphomolybdate has two great advantages. First, the precipitate can be washed and collected with great ease on account of its granular nature; and secondly, a high ratio exists between its weight and the weight of its phosphoric acid content, for the weight of the phosphomolybdate is between eight and nine times as great as that of an equivalent amount of magnesium ammonium phosphate. Thus a very considerable error in the weight of the phosphomolybdate would influence but slightly the accuracy with which the phosphoric acid could be determined.

The following research was the result of a conviction that it was possible so to regulate the conditions which determine the composition of the phosphomolybdate as to make it possible to obtain a substance of constant composition.

The first step in the problem was to prepare the precipitate in a state suitable for weighing. For this purpose a washing solution was necessary, in which the precipitate is insoluble, and which subsequently can be completely removed from it. Water decomposes the precipitate, as is well known; nitric acid dissolves it;[1] molybdic acid cannot be removed without washing with some other medium. Ammonium nitrate, on the other hand, neither decomposes nor dissolves the precipitate,[2] and it can be completely volatilized at a comparatively low temperature. Evidently, if the precipitate could be heated to the point at which ammonium nitrate decomposes, no better medium for washing could be obtained than a solution of this salt. Such proved to be the case. The phosphomolybdate, when washed with a 10 per cent solution of ammonium ni-

[1] About a gram of the precipitate was digested for some time with 1 per cent nitric acid in the cold. The solution, after filtration and evaporation, left a residue. Stronger acid gave a yellow solution. See also Eggertz: J. prakt. Chem., 79, 496.

[2] Stankel found the yellow precipitate to be least soluble in neutral ammonium nitrate. Ztschr. anal. Chem., 31, 353.

trate, can be heated to constant weight at 300° without decomposition. Since ammonium nitrate is converted into nitrous oxide and water at 220°±,[1] the decomposition of this salt must be complete at 300°. This is evident from the following experiments.

A solution of calcium phosphate in nitric acid was added to an excess of the ordinary molybdic acid solution,[2] both solutions being at the room temperature. After being thoroughly washed by decantation with 10 per cent ammonium nitrate, the precipitates were collected in porcelain Gooch crucibles. The crucibles with the precipitates were heated in a small copper air-bath, 12 cm. in diameter and 13 cm. in height, and jacketed with one thickness of heavy asbestos paper. With such a bath a temperature of 300° is obtainable by means of a good Bunsen burner. Copper oxidizes rapidly at the above temperature, and the bath becomes coated both inside and out with scales of copper oxide, which are easily detached,—a source of contamination of the precipitate unless great care is exercised. A porcelain air-bath is exempt from the above disadvantages, but, on the other hand, is very liable to breakage at the high temperature employed, as well as being much less easily heated to the desired temperature. Where electricity is available an electric air-bath of either glass or porcelain affords a superior means of heating the precipitate. The precipitates were cooled in desiccators containing sulphuric acid, for it was found that they gradually gained in weight in the desiccator when fused calcium chloride was used as a drying agent.[3]

At temperatures below 290° the precipitates lost in weight so slowly that the attempt to obtain constant weight was given up. At 290° the weight became constant within a little more than a milligram in 3 grams, after three hours' heating, while at 300° this result was reached even more quickly. Where saving of time is an object the latter temperature is preferable. However, care must be exercised that the temperature does not much exceed 300°, since decomposition of the pre-

[1] Dammer: Handbuch der anorg. Chem., II., 2, 272.

[2] Made by dissolving 150 grams of ammonium molybdate in 1 liter of water and pouring the solution into 1 liter of nitric acid of the sp. gr. 1.2.

[3] The fact that the precipitate is very hygroscopic was noted by Finkener. Ber. d. chem. Ges., 11, 1638.

cipitate, accompanied by blackening and loss of weight, sets in. Up to 325° the precipitate retains its yellow color which is considerably darker at high temperatures than the lemon-yellow color which it possesses when cold.[1]

*Table I.*

| Period of each heating. | Temperature. Centigrade. | Weight of precipitate I. | Weight of precipitate II. | Weight of precipitate III. | Weight of precipitate IV. | Weight of precipitate V. | Weight of precipitate VI. |
|---|---|---|---|---|---|---|---|
| Hrs. | | Grams. | Grams. | Grams. | Grams. | Grams. | Grams. |
| 3 | 290° | 2.8952 | 2.8968 | .... | .... | .... | .... |
| 18 | 290° | 2.8945 | 2.8955 | .... | .... | .... | .... |
| 18 | 290° | .... | .... | 2.8942 | 2.8946 | .... | .... |
| 18 | 290° | .... | .... | 2.8935 | 2.8938 | .... | .... |
| 1 | 300° | .... | .... | .... | .... | 2.9107 | 2.9149 |
| 2 | 300° | .... | .... | .... | .... | 2.9097 | 2.9149 |
| 18 | 290° | .... | .... | .... | .... | 2.9092 | 2.9144 |

A standard solution of phosphoric acid was prepared as follows: Disodium phosphate was purified by five recrystallizations, in platinum vessels, with water which had been condensed in a block-tin condenser. About 25 grams of the crystals were dissolved in 500 cc. of water. As soon as possible after the solution had been prepared, it was analyzed, first by evaporation of weighed portions of the solution in platinum crucibles and ignition of the residue, then by precipitation of the phosphoric acid by slowly dropping magnesia mixture into fresh portions of the solution after each had been diluted to a volume of 75 cc. The agreement of the results obtained by the two methods leaves no doubt as to the strength of the solution.

*Table II.*

| Number of analysis. | Weight of solution. Grams. | Weight of $Na_4P_2O_7$. Gram. | Weight of $Mg_2P_2O_7$. Gram. | Per cent $P_2O_5$. |
|---|---|---|---|---|
| 1 | 25.262 | 0.4358 | .... | 0.9202 |
| 2 | 39.808 | 0.6867 | .... | 0.9202 |
| 3 | 40.550 | 0.6991 | .... | 0.9197 |
| | | | Average, | 0.9200 |
| 4 | 25.436 | .... | 0.3669 | 0.9197 |
| 5 | 30.499 | .... | 0.4400 | 0.9198 |
| | | | Average, | 0.9198 |

[1] Eggertz also found that at 325° the precipitate is still yellow. J. prakt. Chem., 79, 496.

The first experiments with the ammonium phosphomolybdate were carried out by precipitation of the phosphoric acid in the above solution by means of the solution of molybdic acid generally recommended for the purpose (see foot-note, page 300). Weighed portions of about 10 cc. of the phosphate were diluted to 50 cc. (*i. e.* so that the solution contained about 1 decigram of phosphoric anhydride in 50 cc.), and were then added to about 100 cc. of the molybdic acid solution. Both solutions were at the room temperature. Obviously this method is better than pouring the molybdic acid into the phosphate, for the mechanical inclusion of molybdic acid solution would have far less effect upon the weight of the precipitate than the inclusion of the phosphoric acid. As a matter of fact, several experiments carried out in the reverse manner yielded anomalous results which have not yet been investigated. The liquid was immediately colored yellow, although precipitation began in most cases only after several seconds and proceeded slowly. As would be expected, precipitation was hastened by stirring, and in fact, incomplete precipitation resulted in some cases where vigorous stirring was omitted. Within an hour in the cold the precipitate had settled in great part, leaving a solution which was still colored slightly yellow and which continued to deposit a precipitate for several hours longer. After standing at least sixteen hours the precipitates were washed with 10 per cent ammonium nitrate and collected in weighed porcelain Gooch crucibles. This operation is easily carried out, for although the precipitate adheres to the sides of the containing vessel to a considerable extent it can be easily detached by friction, best with a rubber "policeman." The granular nature of the precipitate aids very materially in the washing and transferring. The precipitates were finally heated for eighteen hours at 290° before being weighed.

The ammonium nitrate was found to be free from chloride and sulphate by the usual tests. Furthermore, 10 cc. of the washing solution were evaporated to dryness in a platinum crucible and the residue then heated to 290° in the air-bath. The crucible gained 0.0002 gram, hence the nitrate must have been essentially free from alkalies also.

*Table III.*

| Number of analysis. | Weight of solution. Grams. | Weight of $P_2O_5$ calculated.[1] Gram. | Molybdic acid. cc. | Weight of precipitate. Grams. | Per cent of $P_2O_5$ in precipitate. |
|---|---|---|---|---|---|
| 6 | 10.0895 | 0.09282 | 100 | 2.4803 | 3.7425 |
| 7 | 10.1076 | 0.09299 | 100 | 2.4842 | 3.7432 |
| 8 | 10.1571 | 0.09344 | 100 | 2.4982 | 3.7404 |
| 9 | 10.1240 | 0,09314 | 100 | 2.4880 | 3.7436 |
| 10 | 10.1975 | 0.09382 | 90 | 2.5088 | 3.7396 |
| 11 | 10.1050 | 0.09297 | 90 | 2.4864 | 3.7389 |
| 12 | 10.1350 | 0.09324 | 80 | 2.4902 | 3.7453 |
| 13 | 10.1340 | 0.09323 | 80 | 2.4894 | 3.7443 |
| | | | | Average, | 3.7422 |

In Analysis 12, 0.5 cc., and in Analysis 13, 1 cc. of concentrated nitric acid was added to the phosphate before precipitation. Evidently such slight changes in the conditions as those indicated produce no appreciable effect.

Since the formula $(NH_4)_3PO_4.12MoO_3$ demands 3.783 per cent of phosphoric anhydride, this formula cannot represent the composition of the precipitate obtained as above. The cause of the discrepancy could be determined only by analyzing the precipitate.

New solutions of phosphoric acid, of such a strength that 25 cc. contained very nearly 1 decigram of phosphoric anhydride, were now prepared by dissolving calcium phosphate in nitric acid. Portions of 25 cc. were precipitated with molybdic acid under exactly the same conditions as before. From the weights of the precipitates so obtained were calculated the strengths of the solutions, assuming the percentage of phosphoric anhydride to be 3.742. Since in no case did the weights of the precipitates obtained from the same solution vary more than 0.1 per cent, this method must afford an accurate estimation of the phosphoric acid.

A number of the precipitates were then analyzed for ammonia as follows: The precipitate was transferred from the crucible to a retort by means of a stream of water from a wash-bottle, an operation easily accomplished since the precipitate showed no tendency to adhere to the crucible. To the tubu-

[1] In calculating the weight of phosphoric anhydride the result obtained by evaporation of the solution was used.

lature of the retort was fitted a separating-funnel which served to introduce a strong solution of sodium hydroxide without danger of loss of ammonia. The ammonia was then determined by distillation into N/5 hydrochloric acid in the usual way.

*Table IV.*

| Number of analysis. | Weight of precipitate. Grams. | Weight of $(NH_4)_2O$. Gram. | Per cent of $(NH_4)_2O$. |
|---|---|---|---|
| 14 | 2.8916 | 0.1161 | 4.016 |
| 15 | 2.8938 | 0.1164 | 4.022 |
| 16 | 2.4937 | 0.1006 | 4.034 |
| | | Average, | 4.024 |

Since it was possible that the precipitate contained water as well as molybdenum trioxide, the water was determined by combustion of the total hydrogen in several samples. From the weight of water found was subtracted that corresponding to 4.024 per cent of ammonium oxide.

*Table V.*

| Number of analysis. | Weight of precipitate. Grams. | Weight of water. Gram. | Weight of water equivalent to 4.024 per cent $(NH_4)_2O$. Gram. | Difference. Gram. | Per cent of water. |
|---|---|---|---|---|---|
| 17 | 2.0668 | 0.1169 | 0.1149 | 0.0020 | 0.097 |
| 18 | 2.2310 | 0.1259 | 0.1241 | 0.0018 | 0.074 |
| 19 | 2.9017 | 0.1639 | 0.1613 | 0.0026 | 0.090 |
| 20 | 3.4095 | 0.1915 | 0.1896 | 0.0019 | 0.056 |
| | | | | Average, | 0.079 |

The sum of phosphoric acid, ammonia, and water is 7.843 per cent. The remainder, 92.16 per cent, can be due to molybdic acid only. Below are tabulated the results obtained experimentally and those calculated from the formula $(NH_4)_3PO_4.12MoO_3$.

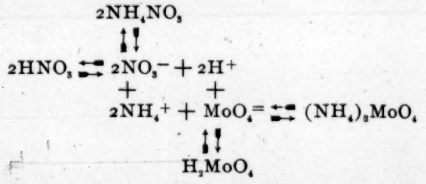
| | Calculated for $(NH_4)_3PO_4.12MoO_3$. | Found. |
|---|---|---|
| $P_2O_5$ | 3.783 | 3.742 |
| $(NH_4)_2O$ | 4.167 | 4.024 |
| $MoO_3$ | 92.06 | 92.16 |
| $H_2O$ | .... | 0.079 |

To explain the discrepancy between the experimental and theoretical percentages of phosphoric anhydride by assuming other stoichiometric relations between phosphoric anhydride and molybdenum trioxide in the precipitate, would lead to an extremely complicated and impossible formula. Such an assumption is, however, unnecessary. The solution from which precipitation takes place contains a large excess of the precipitant, hence nothing is more probable than that the precipitate carries down molybdic acid in excess of the theoretical quantity. If we allow 24 $MoO_3$ for each $P_2O_5$, there are required by 3.742 per cent of the latter 91.08 per cent of the former, while the corresponding percentage of ammonia is 4.123. The extent of the occlusion, 1.08 per cent, is by no means an impossible quantity. The low experimental result for ammonia is probably due to loss of ammonia by the precipitate at the high temperature to which it was subjected, or perhaps even at ordinary temperature while in contact with the strongly acid solution from which it was precipitated. The substitution of a hydrogen atom for an ammonium radical might be expected to have no marked effect upon the color of the compound. This explanation will also account for the presence of a portion of the water. The difference between the experimental and theoretical percentages of ammonium oxide, 0.099, is equivalent to 0.034 per cent of water, nearly one-half the total quantity found. The remainder may be easily accounted for by the well-known difficulty of obtaining a "blank" determination of water in combustion, and by the possibility that even at 300° the precipitate retained a trace of moisture.

Quite recently T. W. Richards has shown that the carrying down of foreign substances by precipitates is not mechanical inclusion of these substances but rather the result of a law of distribution of the portion of these substances existing in an electrically neutral condition, between the solution and the precipitate at the moment of formation. Obviously, he points out, any change in the substances present in solution which tends to diminish the concentration of the group under consideration, tends to diminish the amount occluded. This has been found to hold true in the cases of the occlusion of iron

and chromium salts by barium sulphate[1] and of magnesium oxalate by calcium oxalate.[2]

In the present case we can represent the equilibria in the solution by the following scheme :




If, then, the occlusion is due to undissociated molybdic acid, an increase in the concentration of either the hydrogen or the molybdic ion should produce an increase in the extent of the occlusion ; while, if ammonium molybdate is the primary cause, an increase in the concentration of either the ammonium or the molybdic ion or a decrease in the concentration of the ionized hydrogen should result in increased weight of the precipitate.

One hundred cc. of molybdic acid solution is more than double the amount theoretically necessary to combine with 1 decigram of phosphoric anhydride. It has been shown already (Table III.) that small variations in the quantity used produce no appreciable effect upon the weight of the phosphomolybdate. If 50 cc. are used, *i. e.*, a slight excess, precipitation is incomplete. Filtration was carried out after twenty-four hours, but the filtrate deposited a large amount of precipitate as soon as the ammonium nitrate of the washing solution was mixed with it. After standing twenty-four hours longer, the filtrate and wash-waters were filtered, and again a further addition of ammonium nitrate produced a precipitate.

Seventy-five cc. of precipitant also were found insufficient to produce complete precipitation, but the filtrate was completely freed from phosphoric acid by the ammonium nitrate of the washing solution. In this experiment (Analysis 21)

[1] Proc. Am. Acad., **38**, 377.
[2] *Ibid.*, **36**, 377.

the first filtration yielded 2.8568 grams, the second 0.0387 gram of precipitate. In another case (Analysis 22) 100 cc. of 10 per cent ammonium nitrate were added some time after precipitation. Complete precipitation was the result, as also in Analyses 23 and 24, where the same amount of ammonium nitrate was added to the molybdic acid before precipitation.

*Table VI.*

| No. of analysis. | Molybdic acid. cc. | Weight of precipitate. Grams. | Weight of $P_2O_5$ calculated. Gram. | Per cent $P_2O_5$. | Weight of $(NH_4)_2O$. Gram. | Per cent of $(NH_4)_2O$. |
|---|---|---|---|---|---|---|
| 21 | 100 | 2.8955 | 0.1083 | 3.740 | .... | .... |
| 22 | 100 | 2.8928 | 0.1083 | 3.743 | 0.1171 | 4.049 |
| 23 | 100 | 2.9004 | 0.1086 | 3.744 | .... | .... |
| 24 | 100 | 2.9026 | 0.1086 | 3.742 | .... | .... |
| | | | | Average, 3.742 | | |

In these experiments the effect of ammonium nitrate in decreasing the solubility of the precipitate is marked, but from the fact that the composition of the precipitate is essentially identical with that obtained in Table IV., and is the same whether the ammonium nitrate is added before or after the precipitate is formed, it is evident that it had little influence upon the occlusion. This is to be expected, for the molybdic acid solution itself contained a large amount of ammonium salt (about 60 grams of ammonium nitrate in a liter).

In the following table are given the results obtained by the use of larger quantities of molybdic acid. Naturally no difficulty was experienced through incomplete precipitation:

*Table VII.*

| No. of analysis. | Molybdic acid. cc. | Weight of precipitate. Grams. | Weight of $P_2O_5$ calculated. Gram. | Per cent $P_2O_5$. | Weight of $(NH_4)_2O$. Gram. | Per cent $(NH_4)_2O$. |
|---|---|---|---|---|---|---|
| 25 | 200 | 2.9046 | 0.1083 | 3.728 | 0.1189 | 4.093 |
| 26 | 200 | 2.9044 | 0.1083 | 3.728 | .... | .... |
| 27 | 200 | 2.9049 | 0.1083 | 3.728 | .... | .... |
| 28 | 200 | 2.9042 | 0.1083 | 3.729 | .... | .... |
| | | | | Average, 3.728 | | |
| 29 | 300 | 2.9409 | 0.1094 | 3.721 | | |

These results support the foregoing hypothesis of co-precipitation in a striking manner. If the water content of these precipitates be neglected, the percentage of molybdenum trioxide is in both cases very nearly 92.18. Since 3.728 and 3.721 per cent of phosphoric anhydride correspond to 90.73 and 90.56 per cent of molybdenum trioxide, respectively, the occlusion in the two cases amounts to 1.4 and 1.6 per cent. Evidently occlusion increases with the concentration of the molybdate but at a much slower rate. Each decigram of phosphoric anhydride requires theoretically about 35 cc. of molybdic acid solution, hence an excess of 160 cc. of molybdic acid gives a precipitate containing 3.728 per cent of phosphoric anhydride. If the excess of molybdic acid is 260 cc. the percentage is 3.721, while with an excess of from 50 to 70 cc. it is 3.742 (Table III). Here are sufficient data for computing the percentage of phosphoric anhydride in any precipitate formed under the conditions which have been considered. The curve given on page 314 embraces all points corresponding to an excess of between 60 and 260 cc. of molybdic acid.

It has been shown that the chief effect of ammonium nitrate is to diminish the solubility of the precipitate. Although in Analyses 21 to 24 no influence was exerted on the composition of the precipitate by ammonium nitrate, it was interesting to determine its effect in the presence of more molybdic acid. In Analyses 30 to 33, 100 cc. of a 10 per cent solution of ammonium nitrate were added to the molybdic acid solution before precipitation, and in Analyses 34 to 39, 10 grams of the salt were dissolved in each 100 cc. of the molybdic acid. The differences between these results and those in Table IV. are of negligible magnitude. In the presence of larger quantities of molybdic acid, however, the effect of ammonium nitrate on the composition of the precipitate becomes more marked. In Analyses 40 and 41, 10 grams of ammonium nitrate were dissolved in the molybdic acid, in Analyses 42 and 43, 100 cc. of 20 per cent ammonium nitrate solution were added. Hence the results are comparable with those of Table VII., where the conditions were exactly the same except that the ammonium nitrate was omitted. The difference in the percentage

of phosphoric anhydride, though slight (—0.005 per cent), is large enough to show conclusively that the occlusion increases with the concentration of the ionized ammonium.

*Table VIII.*

| No. of analysis. | Molybdic acid. cc. | Weight of precipitate. Grams. | Weight of $P_2O_5$ calculated. Gram. | Per cent $P_2O_5$. | Weight of $(NH_4)_2O$. Gram. | Per cent of $(NH_4)_2O$. |
|---|---|---|---|---|---|---|
| 30 | 100 | 2.8908 | 0.1083 | 3.746 | 0.1159 | 4.013 |
| 31 | 100 | 2.8941 | 0.1083 | 3.742 | .... | .... |
| 32 | 100 | 2.8954 | 0.1083 | 3.740 | .... | .... |
| 33 | 100 | 2.8975 | 0.1083 | 3.737 | 0.1166 | 4.024 |
| 34 | 100 | 2.8952 | 0.1083 | 3.740 | .... | .... |
| 35 | 100 | 2.8956 | 0.1083 | 3.740 | 0.1173 | 4.052 |
| 36 | 100 | 2.8927 | 0.1083 | 3.743 | 0.1182 | 4.085 |
| 37 | 100 | 2.8938 | 0.1083 | 3.742 | .... | .... |
| 38 | 100 | 2.8945 | 0.1083 | 3.741 | 0.1170 | 4.041 |
| 39 | 100 | 2.8955 | 0.1083 | 3.740 | .... | .... |
| | | | Average, | 3.741 | Average, | 4.043 |
| 40 | 200 | 2.9100 | 0.1083 | 3.721 | .... | .... |
| 41 | 200 | 2.9075 | 0.1083 | 3.724 | 0.1179 | 4.054 |
| 42 | 200 | 2.9187 | 0.1086 | 3.721 | .... | .... |
| 43 | 200 | 2.9142 | 0.1086 | 3.727 | .... | .... |
| | | | | Average, 3.723 | | |

Where the excess of molybdic acid is not too large, the addition of ammonium nitrate before precipitation is a distinct advantage, for it not only hastens the reaction but also assures complete precipitation. The following experiments were carried out with molybdic acid containing 100 grams of ammonium nitrate per liter. In Analyses 46 to 48 it was found possible to reduce the period of standing to one-tenth that necessary in the absence of ammonium nitrate. The filtrate in Analysis 44 became turbid upon standing, while that in Analysis 45 was cloudy :

*Table IX.*

| Number of analysis. | Molybdic acid. cc. | Period of standing. Minutes. | Weight of precipitate. Grams. | Weight of $P_2O_5$ calculated. Gram. | Per cent of $P_2O_5$. |
|---|---|---|---|---|---|
| 44 | 100 | 15 | 2.8946 | 0.1086 | .... |
| 45 | 100 | 30 | 2.8993 | 0.1086 | .... |
| 46 | 100 | 60 | 2.9014 | 0.1086 | 3.743 |
| 47 | 100 | 120 | 2.8991 | 0.1086 | 3.746 |
| 48 | 100 | 120 | 2.9019 | 0.1086 | 3.743 |

If ammonium molybdate is the substance occluded by the precipitate we should expect that a diminution in the concentration of the ionized hydrogen, by increasing the dissociation of the molybdic acid, would bring about an increase in this occlusion. This proved to be the case, for in Analyses 49 and 50, in which one-half the usual excess of nitric acid was present in the molybdic acid solution, the precipitates were over a centigram heavier than before. It was found impossible to study the action of larger quantities of nitric acid because an amount sufficient to be noticeable in its effect produced incomplete precipitation. For instance, in Analyses 51 and 52, 5 cc. of concentrated nitric acid were added to the molybdic acid. Here the filtrates were yellow, showing that precipitation was not even approximately complete.

*Table X.*

| No. of analysis. | Molybdic acid. cc. | Weight of precipitate. Grams. | Weight of $P_2O_5$ calculated. Gram. | Per cent of $P_2O_5$. | Weight of $(NH_4)_2O$. Gram. | Per cent of $(NH_4)_2O$. |
|---|---|---|---|---|---|---|
| 49 | 100 | 2.9149 | 0.1083 | 3.715 | 0.1178 | 4.042 |
| 50 | 100 | 2.9097 | 0.1083 | 3.722 | .... | .... |
| 51 | 100 | 2.8365 | 0.1083 | .... | .... | .... |
| 52 | 100 | 2.7916 | 0.1083 | .... | .... | .... |

When a smaller amount of nitric acid and an increased amount of ammonium nitrate acted together, their combined influence was very much larger than that of either alone. In Analyses 53 to 56 the results were obtained with a molybdic acid solution containing half the usual acid and 20 grams of ammonium nitrate in each 100 cc.

*Table XI.*

| No. of analysis. | Molybdic acid. cc. | Weight of precipitate. Grams. | Weight of $P_2O_5$ calculated. Gram. | Per cent of $P_2O_5$. | Weight of $(NH_4)_2O$. Gram. | Per cent of $(NH_4)_2O$. |
|---|---|---|---|---|---|---|
| 53 | 100 | 2.9208 | 0.1083 | 3.708 | .... | .... |
| 54 | 100 | 2.9202 | 0.1083 | 3.708 | 0.1184 | 4.054 |
| 55 | 200 | 2.9525 | 0.1083 | 3.668 | .... | .... |
| 56 | 200 | 2.9531 | 0.1083 | 3.667 | 0.1203 | 4.074 |

In Analysis 56 the ammonia content demanded by 3.667 per cent of phosphoric anhydride is 4.040, while that found experimentally was 4.074. The occlusion in this analysis is

at its maximum, and since the excess of ammonia could have come only from the occluded substance, here is additional proof that this substance is ammonium molybdate.

One other condition should influence the composition of the precipitate, the dilution at which precipitation takes place. In many of the foregoing experiments the molybdic acid was diluted to double its original volume with ammonium nitrate (Analyses 30, 31, 42 to 48). Here no appreciable effect was produced. In Analyses 57 and 58 the phosphate was diluted so that 1 decigram of phosphoric anhydride was contained in 100 cc. of water. Precipitation was incomplete in these cases. When diluted with 10 per cent ammonium nitrate solution to the same volume, the phosphate yielded results identical with those obtained with stronger solutions (Analyses 59 and 60). Evidently the effect of dilution, if appreciable, is neutralized by the large amount of ammonium nitrate.

*Table XII.*

| Number of analysis. | Molybdic acid. | Weight of precipitate. | Weight of $P_2O_5$ calculated. | Per cent of $P_2O_5$. | Weight of $P_2O_5$ in filtrate calculated. |
|---|---|---|---|---|---|
| | cc. | Grams. | Gram. | | Gram. |
| 57 | 100 | 2.8569 | 0.1083 | .... | 0.0014 |
| 58 | 100 | 2.8566 | 0.1083 | .... | 0.0014 |
| 59 | 100 | 2.4810 | 0.09282 | 3.741 | .... |
| 60 | 100 | 2.4775 | 0.09273 | 3.743 | .... |

Since the concentration of the molybdic acid is always very large, even after precipitation is complete, and since under all conditions the formation of the precipitate is gradual, the rate at which the phosphate is added to the molybdate should have no marked effect. In Analysis 61 the phosphate was added in portions of about 1 cc., and the greater part of the precipitate from each portion was allowed to form before further addition, while in Analysis 62 the phosphate was added drop by drop from a burette. About fifteen minutes were taken for each precipitation. In order to hasten precipitation, 50 cc. of 20 per cent ammonium nitrate were added to the molybdic acid before precipitation. This has been shown already to have no appreciable effect upon the composition of the precipitate except where a large excess of molybdic acid is pres-

ent. The results of these experiments are essentially identical with those obtained by rapid addition of the phosphate.

*Table XIII.*

| Number of analysis. | Molybdic acid. | Weight of precipitate | Weight of $P_2O_5$ calculated. | Per cent of $P_2O_5$. |
|---|---|---|---|---|
| | cc. | Grams. | Gram. | |
| 61 | 100 | 2.9006 | 0.1086 | 3.744 |
| 62 | 100 | 2.8992 | 0.1086 | 3.746 |

It was interesting to determine whether occlusion takes place wholly at the time of precipitation or while the precipitate is standing in contact with the solution from which it is precipitated. In two experiments precipitation was carried out in the presence of an excess of 60 cc. of molybdic acid and much ammonium nitrate; then, after the lapse of an hour, 100 cc. more were added and the whole allowed to stand an hour before filtration.

*Table XIV.*

| Number of analysis. | Weight of precipitate. | Weight of $P_2O_5$ calculated. | Per cent of $P_2O_5$. |
|---|---|---|---|
| | Grams. | Gram. | |
| 63 | 2.9116 | 0.1086 | 3.730 |
| 64 | 2.9113 | 0.1086 | 3.730 |

Precipitation must have been complete at the end of the first hour (see Analyses 46 to 48), so that the observed decrease in the percentage of phosphoric anhydride below that when the excess of molybdic acid is 60 cc. (—0.012 per cent) must have been due to increased occlusion owing to the second addition of molybdic acid.

In all probability, then, occlusion takes place in two stages, at the time of precipitation and while the precipitate is standing in contact with the solution. The first should be dependent on the concentration of the substances in the solution at the time of precipitation; the second evidently depends upon the conditions which exist in the solution after precipitation and also upon the time during which the precipitate is allowed to stand before filtration. This is shown by the following experiments, in which the precipitates remained five days in contact with the solution.

*Table XV.*

| Number of analysis. | Molybdic acid. cc. | Weight of precipitate. Grams. | Weight of $P_2O_5$ calculated. Gram. | Per cent of $P_2O_5$. |
|---|---|---|---|---|
| 65 | 80 | 2.2709 | 0.0846 | 3.726 |
| 66 | 80 | 2.2733 | 0.0846 | 3.722 |
| 67 | 160 | 2.2938 | 0.0846 | 3.689 |
| 68 | 160 | 2.2908 | 0.0846 | 3.693 |

During this time the precipitates with the smaller excess of molybdic acid increased in weight 0.5 per cent, those with the larger excess, 1 per cent. Obviously, although the gain in weight per day is very small, 0.1 per cent in one case, 0.2 per cent in the other, the filtration should be carried out as soon as possible after the precipitation is complete.

The results of this investigation are as follows:

1. The precipitate formed by the addition of a solution of a phosphate to an excess of molybdic acid has the formula $(NH_4)_3PO_4.12MoO_3$.

2. The precipitate occludes ammonium molybdate at the moment of precipitation, and later adsorbs more of this salt. The amount of the latter varies considerably with the concentration of the undissociated ammonium molybdate in solution and the time during which the precipitate remains in contact with the solution.

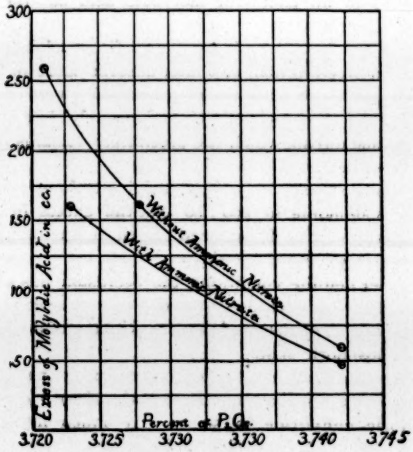
3. This occluded ammonium molybdate loses the greater part of its ammonia at 290°, so that the excess in weight of the precipitate, after it has been heated to this temperature, is due to molybdenum trioxide.

4. Under definite conditions the occlusion has a constant value. This has been determined for various conditions, so that the weight of the precipitate can be used for the estimation of phosphoric acid.

5. The conditions most favorable to exact analysis are as follows: The solution should contain about 1 decigram of phosphoric anhydride in 50 cc. If much nitric acid is present, the greater part should be removed by evaporation. The phosphate should be poured, with vigorous stirring, into a quantity of the usual molybdic acid solution at least 50 cc. in excess of the amount theoretically necessary to precipitate

the phosphoric acid, both solutions being at the room temperature. After standing about sixteen hours the precipitate should be washed with 10 per cent ammonium nitrate solution, transferred to a Gooch crucible, and heated to 300° for at least two hours. From the weight of the precipitate the excess of molybdic acid can be found by first making an approximate estimation of the phosphoric anhydride. The exact percentage of phosphoric anhydride can then be found from the following curve.

In order to hasten precipitation, ammonium nitrate may be added. Ten grams for 100 cc. of molybdic acid is sufficient to produce complete precipitation within one hour. The percentages of phosphoric anhydride in precipitates obtained in this way are only slightly different from those obtained without the use of ammonium nitrate.




It must be clear from this paper that the accuracy and rapidity with which phosphoric acid can be determined by weighing the ammonium phosphomolybdate are such as to

entitle this method to a place among the standard analytical processes. For, by conducting the precipitation in the presence of a large amount of ammonium nitrate and heating the precipitate to 300°, results accurate within 0.1 per cent can be obtained within four hours.

CHEMICAL LABORATORY OF SWARTHMORE COLLEGE, SWARTHMORE, PA.,
June 23, 1902.

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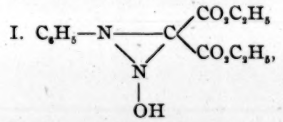
Contributions from the Chemical Laboratory of Union College.

## ON AN ACID DERIVATIVE OF ETHYL ANILINOMALONATE.

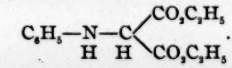
BY RICHARD SYDNEY CURTISS.

In a former paper[1] I gave a brief description of the action of nitrous acid on ethyl anilinomalonate, by which was produced an oil possessing acid properties, to which the formula

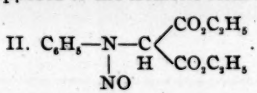


ethyl $\alpha$-phenyloxydiazomalonate was tentatively given.

The substance has since been prepared in larger quantities and studies made of its potassium, sodium, and ammonium salts, and also of the effect of heat, and of acetic anhydride upon it. Reduction by zinc and acetic acid liberates nitrogen as ammonia and yields ethyl anilinomalonate,



The results of tests of its electrical conductivity and the rapidity with which it forms a salt with alcoholic potash are the best indications yet found for the above constitutional formula, I., as opposed to the isomeric form :



[1] This JOURNAL, 23, 509.

(Ethyl nitrosoanilinomalonate.) The precipitation of the ammonium salt by addition of dry ammonia gas to the body, in solution in a non-ionizing solvent, is soon to be tried.[1] The body gives with ferric chloride solution a deep-red color, and does not give the Liebermann nitroso reaction.

A detailed account of the experimental work follows:

*Preparation of the Acid Oil.*—The following conditions, closely observed, yielded the best results: Twenty grams of finely powdered ethyl anilinomalonate, prepared by the method already described,[2] are suspended in 30 cc. of water containing 4.8 grams of sulphuric acid (theory, 4 grams). This is shaken in a glass-stoppered bottle with a solution of 5.9 grams of sodium nitrite (theory, 5.5 grams) in 50 cc. of water. The latter solution is added in small quantities, with violent shaking, while the temperature is kept at 12° to 16° by frequent immersion in ice-water. The reaction begins immediately after the addition of the nitrite. The nitrous acid is rapidly and completely absorbed, the particles of ester becoming oily. After one-half of the salt has been added, the oily mass begins to break up and to separate into a fine emulsion. After all of the nitrite has been added the shaking is continued for ten minutes, and the mass is then allowed to settle. The aqueous solution is separated in a funnel from the oil and extracted repeatedly with ether. The oil is then added to the latter and washed thoroughly with cold water, then with a little sodium carbonate solution to remove all traces of mineral acids, and lastly very thoroughly with cold water. After drying over calcium chloride the ether is distilled off in a vacuum at 0°. The product is best kept in a desiccator over sulphuric acid in a dark room.

The utmost care is requisite in carrying out the above operation, as very slight variations in the quantities of the reagents, in the temperature, or in the time consumed in the operation, as well as in the degree of washing, have a marked effect on the purity of the oil and its keeping qualities.

Thus prepared, the product is a thick, clear, amber oil, of slightly reddish tint by transmitted light, and possessing a

[1] Hantzsch and Dollfus: Ber. d. chem. Ges., 35, 226.
[2] Curtiss: This JOURNAL, 19, 693.

bitter taste. It is easily soluble in benzene, ether, alcohol, chloroform, and glacial acetic acid, very slightly soluble in ligroin and in water. Strong bases dissolve it easily with formation of yellow solutions. Sodium carbonate solution appears to act but slowly on it. Heat and sunlight readily decompose it with evolution of gases (oxides of nitrogen) and formation of a thick red oil. It may sometimes be kept from four to six weeks over sulphuric acid, with little change. On the other hand, the slightest traces of impurity or even neutral substances (grains of glass or sand, etc.) will decompose it quickly.

The molecular weight determinations of the oil, as well as the analyses of the sodium and potassium salts, already given,[1] show the substance to have the empirical formula $C_{13}H_{16}O_5N_2$, required for a body of the structure represented by I.

The following tests of the electrical resistance of the oil and its potassium salt were made in absolute alcohol solutions (20 cc.), using the same cell in all experiments (with dull platinized electrodes 1 cm. apart) immersed in a water-bath provided with a thermostat. The readings were made with a Wheatstone bridge and telephone arrangement, using an alternating current. The sample of oil used was freshly prepared and very carefully purified, and dried in a vacuum over sulphuric acid.

*Experiment I.*

Determination of the resistance of a N/10 solution of potassium hydroxide in absolute alcohol, and the rate of change of the resistance on addition (1) of 0.5 molecule of the acid oil, and (2) a second 0.5 molecule of the acid oil in N/10 solution in absolute alcohol.

[1] This JOURNAL, **23**, 510.

Temperature, 19°.

| Time in minutes. | Readings on Wheatstone bridge. a. (KOH solution.) | b. | Interposed resistance. w. Ohms. | Observed resistance. x. Ohms. | Specific resistance per cc. of solution. k. |
|---|---|---|---|---|---|
| | 501 | 499 | 90 | 89.6 | 1.1115 |
| 0 | (Added 0.5 mol. acid oil, 10 cc.) | | | | |
| 1 | 530 | 470 | 230 | 204 | 0.25296 |
| 1.5 | 520 | 480 | 230 | 212 | 0.26326 |
| 8.5 | 515 | 485 | 230 | 217 | 0.2686 |
| 15.5 | 514 | 486 | 230 | 218 | 0.2703 |
| 17.5 | (Added 2nd 0.5 mol. acid sol., 10 cc.) | | | | |
| 18.5 | 558 | 442 | 730 | 578 | 0.7170 |
| 19.5 | 555 | 445 | 730 | 585 | 0.7258 |
| 22.5 | 554 | 446 | 730 | 588 | 0.7291 |
| 23.5 | 554 | 446 | 730 | 588 | 0.7291 |
| 31.5 | 554 | 446 | 730 | 588 | 0.7291 |
| 47.5 | 554 | 446 | 730 | 588 | 0.7291 |
| 1 hr. 47.0 | 558 | 442 | 730 | 578 | 0.7170 |
| 21 hrs.[1] | 690 | 310 | 730 | 328 | 0.4067 |

*Experiment II.*

Determination of resistance of a N/10 solution of the acid oil in absolute alcohol, after addition of 20 cc. of N/10 potassium hydroxide solution (1 mol.) in absolute alcohol.

Temperature, 19°.

| Time in minutes. | a. | b. | w. | x. | k. |
|---|---|---|---|---|---|
| 10 | 534 | 466 | 700 | 611 | 0.7576 |
| 15 | 535 | 465 | 700 | 608 | 0.7539 |
| 17 hrs. | 490 | 510 | 400 | 420 | 0.5208 |

In this experiment quick readings could not be made directly after the addition of the alkali, owing to a defect in fixing the interposed resistance.

*Experiment III.*

Determination of the resistance of the absolute alcohol used in experiments I. and II.

Temperature, 19°.

| a. | b. | w. | x. | k. |
|---|---|---|---|---|
| 135 | 865 | 11000 | 70481 | 87.393 |

[1] Crystals have separated out in small quantity.

*Experiment IV.*

Determination of the resistance of a N/3 solution of the acid oil in the absolute alcohol used in experiment III. (1.87 gram oil in 20 cc. alcohol).

Temperature, 19°.5.

| a. | b. | w. | x. | k. |
|---|---|---|---|---|
| 284 | 716 | 11000 | 27732 | 34.3875 |

The values of *a* and *b* are the mean of twelve readings taken at intervals of two minutes. No change in the resistance was noticed after the first reading, but the telephone minimum was indistinct.

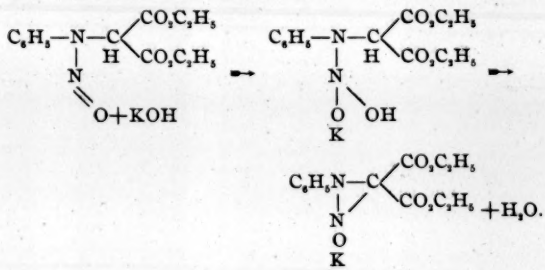
*Experiment V.*

Determination of the resistance of the cell used in the preceding experiments. A N/10 aqueous solution of potassium chloride was used.

Temperature 25°.

| a. | b. | w. | x. | Cell resistance. |
|---|---|---|---|---|
| 490 | 510 | 10 | 10.408 | 0.00124 |

From the above test (I.) it would appear that the oil under consideration is in large part, if not wholly, a true acid (formula I.), as it seems very improbable that a non-acid (formula II.) would change to an acid body instantaneously, or so nearly so, by addition of potassium hydroxide and subsequent splitting off of water, thus:




*Sodium Salt.*—To prepare the sodium salt of the acid oil in

its greatest purity, 18 cc. of a 10 per cent solution of sodium hydroxide (0.2 gram excess of sodium hydroxide) are added, in small portions, to 12.2 grams of the clear amber oil. The canary-yellow salt immediately separates from the oily mixture. The mass is rubbed with a glass rod until it is finely divided and entirely free from oily appearance. The temperature must be kept below 15° during the operation as the aqueous solution of the salt decomposes at ordinary temperatures. At the end of three-quarters of an hour the crystal mass is thoroughly freed from the liquid with the aid of a pump and carefully washed, first with small quantities of ice-water, next with dry ether, then with chloroform. This treatment frees the salt from all alkali and oily impurities and leaves it sufficiently pure for analysis, as the figures already given[1] show. The yield is nearly quantitative.

The sodium salt has the following properties: It forms canary-yellow needles, easily soluble in alcohol, and acetic ether, fairly soluble in ether, and water, slightly so in chloroform. An aqueous solution of the salt soon changes, (probably by hydrolysis and partial decomposition) yielding a light, clear-yellow oil of a peculiarly sweet, penetrating odor, which is unstable and decomposes in a short time, yielding colorless needles, which melt near 112°.

All attempts to recrystallize the sodium salt from solutions in the above solvents result in its partial decomposition. Slow heating, at 70° to 100°, causes the evolution of oxides of nitrogen and the formation of a yellow oil of the peculiar odor mentioned above. When quickly heated it melts at 118° to 122°.

*Regeneration of the Acid Oil from Its Sodium Salt.*—8.75 grams of the pure yellow salt are placed in a separatory funnel with 20 to 25 cc. each of ether and water. Dilute sulphuric acid in the slightest excess is slowly added in small portions, and the mixture well shaken, the temperature being kept below 12° to 14°. The ethereal solution is very thoroughly washed, first with a little sodium carbonate solution then many times with ice-water. The ethereal solution is

[1] *Loc. cit.*

dried over calcium chloride and the ether distilled off in a vacuum at 0°. The product is 7.1 grams of a thick oil, identical in all its properties with the original body from which the sodium salt was formed.

*The Potassium Salt.*—This is best made in an analogous manner and by observing the precautions referred to in the preparation of the sodium derivative. Three-tenths of a gram of potassium hydroxide (theory 0.28 gram) in solution in 2 cc. of ice-water are gradually added to 1.4 grams of the oil, the temperature being kept below 15°. After half an hour of thorough mixing the salt is filtered and washed, as above described. The product is a yellow salt which, if made in more dilute solution, separates out in fine crystal form, having the appearance of orthorhombic sulphur. It melts on quick heating at 118° to 120° with evolution of gas. It is easily soluble in water and absolute alcohol, slightly soluble in chloroform and benzene, insoluble in ligroin. (Analytical results in preliminary report.) If perfectly dry and pure this salt keeps for weeks without decomposition. It is easily decomposed, however, in aqueous solution at ordinary temperatures, more rapidly on heating, yielding apparently the same yellow oil that is formed from the sodium salt under like conditions.

*The ammonium salt* of the acid oil is formed when it is shaken with a slight excess of concentrated ammonium hydroxide, at low temperatures. The body precipitates out as a light-yellow salt, easily soluble in water and ether. It is much less stable than the salts of sodium and potassium. It decomposes in the desiccator over sulphuric acid, and on boiling its ethereal solution, it hydrolyzes, yielding ammonia and a clear amber oil, which possesses the properties of the original substance from which the salt is formed.

*The effect of heat on the acid oil* is to decompose it with evolution of gases, consisting chiefly of nitrogen and nitric oxide, with small quantities of carbon dioxide. A thick, red, neutral oil, which cannot be distilled in a vacuum, is left behind. 9.8 grams of the acid body are placed in a small flask provided with a gas-delivery tube and immersed in a paraffin-bath, the gases evolved being collected over cold water. As

the temperature of the oil is raised to 110° gas begins to be evolved. By gradually increasing the temperature for two hours, from this point to 180°, a steady and rapid flow of gas is maintained. After this time the gas ceases to come off. The contents of the flask weigh 8.5 grams and emit a pungent odor. A small quantity of water is also a product of the decomposition. On analysis, 57 cc. of the gas which escaped were found to consist of

| | cc. |
|---|---|
| NO | 31.5 |
| N | 22.5 |
| $CO_2$ | 3.0 |
| | 57.0 |

From the residual oil in the flask a crystal mass separated on cooling. The mixture was shaken with ether and washed repeatedly with dilute sodium hydroxide solution, and lastly with water. (The alkaline wash-water, when treated with hydrochloric acid and ether, yielded 0.15 gram of a dark oil, smelling strongly of phenols.)

The yellow ethereal solution, dried over calcium chloride and distilled in a vacuum, left 7.3 grams of oil, from which 0.82 gram of needle crystals separated on cooling. This product was purified by boiling a solution of it in absolute alcohol with bone-charcoal, and recrystallizing from the same solvent. It melted constantly at 111°, giving a clear oil, which evolved gases at 200° to 250° and turned dark. The analysis gave the following figures :

0.1669 gram substance gave 18.2 cc. N gas at 19° and 741.4 mm., equivalent to 12.50 per cent.

The substance crystallizes in white, silky needles, insoluble in cold water and sodium hydroxide. It is slightly soluble in hot water and in hydrochloric acid, fairly so in alcohol and ether, easily soluble in acetone and benzene. The oily mother-liquor from the above crystal body could not be distilled in a vacuum. It was treated with aniline, and after twenty-four hours the mixture, on being rubbed up with ether and hydrochloric acid, yielded 3.5 grams of grayish-

white needles. The substance was boiled with bone-charcoal and alcohol (95 per cent). The yellowish-white crystals obtained melted (not sharply) at 110° to 111°. An attempt to further purify this body by treatment with bone-charcoal in 60 per cent alcohol resulted in its decomposition into a yellow oil, with a slight odor of aniline.

*Action of Acetic Anhydride on the Acid Oil.*—Four and two-tenths grams of the pure amber oil mixed with 3 grams of acetic anhydride (2 mol.) was heated in a flask provided with a reverse condenser and calcium-chloride tube, and immersed in a paraffin-bath. At a temperature of 125° to 130° gases are rapidly evolved. The color of the oil does not change within two and a half hours with rise of temperature up to 160°. At the end of three hours the operation was stopped. The contents of the flask had lost 0.8 gram in weight, and from 80 to 90 cc. of gas had been collected over water. On cooling the oil, crystals separate, and an odor of acetic ether was noticed on opening the flask, indicating the loss of an ethoxy group.

The ethereal extract of the oil was washed with a dilute solution of sodium hydroxide, and with water, and dried with calcium chloride. After removing the ether by distillation, 0.9 gram of white crystals were obtained. This product, recrystallized from absolute alcohol and washed with ether, yielded pure, silky, white needles, having a sharp melting-point, 111° to 111°.5, and giving a clear oil. This substance is neutral and is identical in properties and nitrogen content with the body formed by heating the acid oil alone (see p. 322).

Analysis :

| | Found. | |
|---|---|---|
| | I. | II. |
| C | 54.4 | 54.3 |
| H | 4.60 | 4.5 |
| N | 12.47 | .... |

Analyses I. and II. are of samples from different experiments, carried out under like conditions. Two series of molecular weight determinations with this body gave :

*I. By the Boiling-point Method in Pure Benzene.*

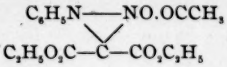
| Determinations. | S. Grams. | L. Grams. | Δ. | Molecular weight M. Found. |
|---|---|---|---|---|
| 1 | 0.0506 | 32.39 | 0°.011 | 379 |
| 2 | 0.1548 | " | 0°.055 | 232 |
| 3 | 0.2543 | " | 0°.093 | 226 |

*II. By the Freezing-point Method in Pure Benzene.*

| Determinations. | S. Grams. | L. Grams. | Δ. | Molecular weight. M. Found. |
|---|---|---|---|---|
| 1 | 0.0807 | 13.07 | 0°.143 | 212 |
| 2 | 0.1524 | " | 0°.262 | 218 |

Analyses of the lower fraction of the gases evolved in the above experiment on gradually raising the temperature of the bath to 93° during one and a half hours showed: Nitrogen, about 76 to 78 per cent by volume; nitric oxide, 20 per cent; carbon dioxide, 2 to 3 per cent. A second fraction obtained by further heating, for two hours, at a temperature of 93° to 130°, contained: nitrogen, 40 per cent; nitric oxide, 55 to 60 per cent; with very little carbon dioxide.

In the first experiment in which the action of acetic anhydride upon the acid oil was tried, a neutral substance was obtained, having much the same crystalline appearance as the above-mentioned body (m. p. 111°). It was easily soluble in chloroform, ether, acetone, and benzene; slightly so in hot water and alcohol; insoluble in ligroin and in cold sodium hydroxide solution. A boiling solution of potassium hydroxide dissolves it slightly, with apparent saponification. It melted at 114°. A molecular weight determination[1] gave the figure 340. The theoretical for an acetyl derivative,



is 322.

After many attempts I have been unable to obtain enough of this body for further study and analysis.

*Reduction of the Acid Oil.*—One and four-tenths grams of oil

[1] This JOURNAL, 23, 511.

in partial solution in 50 per cent acetic acid was treated with granulated zinc. The evolution of gas proceeds very slowly after a few minutes. After standing one-half hour at the room temperature the mixture was gently warmed, when the evolution of gas started again. The solution and suspended oil turned green during the process. Sufficient dilute acetic acid is added from time to time to prevent precipitation of salts, and the whole allowed to stand at the temperature of the room for eighteen hours. It is then neutralized with sodium hydroxide solution and repeatedly extracted with ether. The latter is dried over calcium chloride and distilled off on the water-bath. From the residual oil 0.7 gram of crystals separate on standing a short time. This product was purified by boiling its solution in alcohol with bone-charcoal. Evaporation of the alcohol leaves a thick, clear, light-green oil, which immediately forms a mass of monoclinic crystals on being rubbed with a glass rod (characteristic behavior of ethyl anilinomalonate). The pure body is greenish-white, melts sharply at 44°, is easily soluble in alcohol, ether, chloroform, acetone, and benzene ; fairly soluble in ligroin ; insoluble in water. It reduces cold ammoniacal silver nitrate solution, giving, when heated, a strong silver mirror. It is oxidized by mercuric oxide to ethyl dianilinomalonate,[1]

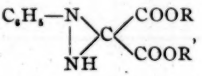
$$\begin{matrix} C_6H_5.NH \\ C_6H_5.NH \end{matrix}\!\!>\!C.(CO_2C_2H_5)_2.$$

The aqueous solution in this reduction experiment, after extraction with ether, was evaporated to dryness. The salt residue, when treated with sodium hydroxide, gave proof of the presence of large quantities of ammonium salts. This, together with the formation of ethyl anilinomalonate, indicates that in the reduction of the acid oil with zinc and acetic acid the nitrogen of the isonitroso (or nitroso) group is split off in the form of ammonia.

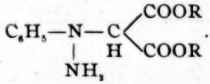
Reduction experiments were also tried with 2.5 per cent sodium amalgam, working in neutral, acid, and alkaline solutions, in the hope of forming an intermediate reduction body

[1] This JOURNAL, 19, 694.

containing both nitrogen atoms, possibly a three-membered ring compound



or a $\beta$-substituted phenylhydrazine derivative,



In one case 0.4 gram of a yellow crystalline body was obtained, which was soluble in acids, sodium hydroxide, and water.

In all the cases of reduction studied, nitrogen is split off in the form of ammonia.

The study of this reduction will be continued. Electrolytic reduction experiments yielded no satisfactory results on preliminary trials.

I am now studying the substitution of positive and negative groups in the benzene ring of this acid oil, to determine the effects on the stability and acid properties of the substance. It is hoped that an analogously constituted body may be obtained, of slightly greater stability, upon which a careful study may be made of the manner in which the molecule breaks up under the influence of heat, alkalies, etc.

I wish to express here my thanks to Professor Bancroft and Dr. Carveth of the Cornell Laboratory of Physical Chemistry, to whom I am greatly indebted, for the facilities of that laboratory placed at my disposal for conducting the physical tests described in this line of work, and especially for valuable suggestions while applying such tests. My thanks are also due Doctors Ebersole, Derby, and Lincoln for the use of the specially purified solvents required in the molecular weight determinations.

UNION COLLEGE, SCHENECTADY, N. Y., May 26, 1902.

# ON THE ACIDS OF THE FAT OF THE CALIFORNIA BAY TREE.

By J. M. Stillman and H. C. O'Neill.

In 1882 we published[1] a summary of a brief examination of the fatty acids of the seeds of the California Bay Tree ( *Umbellularia Californica* in which we presented evidence of the existence of an acid, $C_{11}H_{22}O_2$. The work was interrupted by the departure of one of us (J. M. S.) for residence in the Atlantic States, and by the absorption of our interests in other directions. On account of the anomalous position which the acid named seemed to hold as the only naturally-occurring fatty acid of this series with an odd number of carbon atoms, it seemed to us of importance to investigate more completely this fat, and finding ourselves, after many years, again in a position to pursue the examination, we prepared some time ago a much larger quantity of the fat than was at our disposal in the first examination, and subjected the free acid to repeated distillations. The result of our examination thus has been to satisfy us that in spite of the experimental evidence contained in our previous publication and which seemed to us to warrant the conclusions drawn, we were dealing with a mixture and not a homogeneous acid. That lauric acid is present is certain. It has been isolated by each of us, but it is mixed with other acids from which we had difficulty in separating it by distillation and by other methods, and we were deceived by the constancy of the analytical data obtained in our first examination of the acids and the salts and ethers obtained from them, into the belief that we were dealing with a homogeneous acid.

The reference by Caspari[2] to our former work, in connection with his examination of the fatty acids of *Lindera Benzoin*, seems to render this explanatory note advisable in advance of more complete data.

April 22, 1902.

[1] This Journal, 4, 206.

[2] *Ibid.*, 27, 291.

# REVIEWS.

FIRST BOOK OF QUALITATIVE CHEMISTRY, FOR STUDIES OF WATER SOLUTION AND MASS ACTION. By A. B. PRESCOTT, PH.D., and E. C. SULLIVAN, PH.D., of the University of Michigan. Eleventh edition, entirely rewritten. New York : D. Van Nostrand Co. 1902. Price, $1.50.

The first edition of this book appeared in 1879 and the present edition has been rewritten in the light of the recent views regarding reactions in water solutions. It is to be used as a guide to qualitative analysis and whenever possible the reactions are regarded as reactions of the free ions and explained on this basis. With this exception the book is similar in its general method of presentation to others upon the same subject, each group being treated in order, the general reactions of the separate metals and methods for their separation following in regular order. J. E. G.

ELEMENTARY ORGANIC ANALYSIS. THE DETERMINATION OF CARBON AND HYDROGEN. By F. G. BENEDICT, PH.D., Instructor in Chemistry in Wesleyan University. Easton, Pa. : The Chemical Publishing Co. 1900. Price, $1.00.

As the author justly remarks in his preface, "Perhaps no analytical operation is at once so fundamentally important and exasperatingly vexatious as organic combustion. As a rule, a knowledge of the operation is chiefly obtained by word of mouth" and perhaps even more by bitter experience. There is probably no operation carried out by a student of quantitative analysis which is so dependent upon experience as organic combustion, but the reviewer is heartily in sympathy with the idea of the author who says that "This little manual is presented in the hope that the descriptions of processes here recorded will aid in making this method of analysis more familiar and more satisfactory." The author describes the method of preparation of the various parts of the apparatus and the method of procedure with great care as regards details, and where a number of modifications have been suggested for the same purpose he describes the ones which have given the greatest satisfaction in his experience with over 2,000 combustions.

A careful reading of this little book will no doubt save a beginner in organic analysis many failures and enable him to work more intelligently and independently of the instructor or fellow-students at every step. J. E. G.